

## PATENT ABSTRACTS OF JAPAN

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(54) EVAPORATION FUNCTIONAL PROPOLIS SOLID COMPOSITION, ITS MANUFACTURE, AND ATMOSPHERE IMPROVER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a propolis solid composition that is useful as an atmosphere improver, etc., by having evaporation functionality, and stably imparting a good sense of odor.

SOLUTION: This evaporation functional propolis solid composition contains (A) a raw lump of propolis or the residue of its extract; (B) water or a mixture of water and a water-soluble solvent that can be hydrogen bonded to water; (C) a surfactant; and (D) a hydrophilic macromolecular compound, the contents of (C) and (D) components being respectively 0.01 to 25 pts.wt. and 0.1 to 50 pts.wt. for a total of 100 pts.wt. of (A) and (B) components.

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JAPANESE

[JP,11-089921,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM  
MEANS EXAMPLE

[Translation done.]

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## CLAIMS

## [Claim(s)]

[Claim 1] (A) The evaporation functionality propolis solid constituent with which a propolis original lump and/or its extract residue, the mixture of independent or the water soluble solvent which can carry out hydrogen bond to water and water and a (B) water (C) surfactant, and (D) hydrophilic-property high molecular compound are contained, and the content of per [ of the (A) component and the (B) component ] total quantity 100 weight section and the (C) component is characterized by the content of the (D) component being 0.1 - 50 weight section in 0.01 - 25 weight section.

[Claim 2] (A) The evaporation functionality propolis solid constituent according to claim 1 whose content rates of a component and the (B) component are 1:999-1:2 in a weight ratio.

[Claim 3] (C) The evaporation functionality propolis solid constituent according to claim 1 or 2 which is the macromolecule anionic surface active agent with which the surface active agent of a component contains carboxylate.

[Claim 4] (D) The evaporation functionality propolis solid constituent according to claim 1, 2, or 3 whose hydrophilic high molecular compound of a component is a carrageenan.

[Claim 5] (B) The manufacture approach of the evaporation functionality propolis solid constituent according to claim 1 or 2 which is made to carry out mixed contact of the solution which makes mixture come to carry out the micell dissolution of the (C) surfactant, and the (A) propolis original lump and/or its extract residue of the water soluble solvent which can carry out hydrogen bond to a water independent or water, and water, considers as a distributed condition, adds (D) hydrophilic-property high molecular compound, and is characterized by to carry out homogeneity mixing subsequently to this.

[Claim 6] (C) The manufacture approach according to claim 5 which is the macromolecule anionic surface active agent with which the surface active agent of a component contains carboxylate.

[Claim 7] (D) The manufacture approach according to claim 5 or 6 that the hydrophilic high molecular compound of a component is a carrageenan.

[Claim 8] The ambient atmosphere amelioration agent which consists of an evaporation functionality propolis solid constituent according to claim 1 to 4.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an evaporation functionality propolis solid constituent, its manufacture approach, and an ambient atmosphere amelioration agent. In more detail, this invention has evaporation functionality, and is stabilized, gives good odor feeling, and relates to the ambient atmosphere amelioration agent which consists of the approach and the above-mentioned propolis solid constituent which manufacture efficiently a propolis solid constituent useful as an ambient atmosphere amelioration agent etc., and this thing.

[0002]

[Description of the Prior Art] Conventionally, the propolis known as a natural antibacterial substance, the natural health promotion matter, etc. is the composite of the secondary metabolite represented by the flavonoids which phanerogamaes collected by Arthropoda, such as a honeybee, such as poplar and a pine, produce, and phenols, and the low matter and salivation object which Arthropoda produces. When making this thing edible, if it remains as it is, since it is too much hard and unsuitable to edible, what used as solution food with the extraction method using ethyl alcohol or a liquefied carbon dioxide, or was usually extracted is mixed with water-soluble polysaccharide, and edible is presented as a solid food article which is easy to disassemble with saliva easily.

[0003] However, the above-mentioned extraction method makes the origin the indiscriminate extraction method which uses a good solvent, and since even both the low matter originally considered not to participate in antibacterial ability or a health promotion function is extracted, nonaqueous solubility is emphasized including the component which is not useful, an extract will be in the condition of being hard to eat, and, moreover, it will become unstable with a drainage system solution. Therefore, even when using as a subsistence store generally, there was a problem that it did not escape that an application is restricted remarkably.

[0004] Although the approach of building the product which extracts only water-soluble materials and is easy to eat is also devised by on the other hand contacting a propolis original lump and water in the food field, this approach cannot take out an oil solubility active principle, and there are also few sampling volumes of water-soluble materials, and it cannot be said as the approach which may be satisfied efficiently.

[0005] Under such circumstances, this invention person invented the propolis food constituent using the hydrophilic solution micell of polyol and a fatty-acid-ester system surfactant by the so-called micell extraction method, and its manufacture approach previously as the approach of satisfying both the engine-performance side on a component extract, and the ease of eating (JP,4-66544,B). While the propolis food which is easy to eat is obtained according to this technique, the liquid propolis food which does not make the low matter which is not useful include can be manufactured by the sorting alternative extractor style, taking out the active principle of water-soluble and oil solubility.

[0006] However, by the system, the peculiar odor was emphasized and there was difficulty as a common subsistence store with which contact in the open air serves as a requirement.

[0007] On the other hand, although there are an American product which confined the propolis component extract into the maltose of a low-molecular solid-state, a tablet product infiltrated into the cellulose of nonaqueous solubility as a propolis solid constituent. From the above-mentioned liquid propolis food product, these are not built only with the advantage of being easy to bring, and did not have evaporation functionality, and the odor also suffered misfortune, and the expansion to fields other than food was unsuitable only at it.

[0008]

[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation, it has evaporation functionality, and it is stabilized, gives good odor feeling, and aims at offering the ambient atmosphere amelioration agent which consists of the approach and the above-mentioned propolis solid constituent which manufacture efficiently a propolis solid constituent useful as an ambient atmosphere amelioration agent etc., and this thing.

[0009]

[Means for Solving the Problem] In order that this invention person may attain said purpose, as a result of repeating research wholeheartedly, a propolis original lump and/or its extract residue, The mixture, the surfactant, and the hydrophilic high molecular compound of water or water, and a specific water soluble solvent The solid constituent contained at a predetermined rate, respectively the active principle of the propolis origin which are a natural antibacterial substance and the health promotion matter Have the evaporation functionality of transpiring a minute amount [ every ] continuation target, and it is stabilized, give good odor feeling, and useful as an ambient atmosphere amelioration agent etc., and this propolis solid constituent In the solution which makes the mixture of water or water, and a specific water soluble solvent come to carry out the micell dissolution of the surfactant, carry out homogeneity distribution of a propolis original lump and/or its extract residue, add a hydrophilic high molecular compound to this, and by carrying out homogeneity mixing Based on a header and this knowledge, it came to complete this invention for the ability to manufacture efficiently.

[0010] This invention Namely, a (A) propolis original lump and/or its extract residue, (B) Mixture of the water soluble solvent which can carry out hydrogen bond to a water independent or water, and water, (C) A surfactant and (D) hydrophilic-property high molecular compound are contained. The content of per [ of the (A) component and the (B) component ] total quantity 100 weight section and the (C) component in 0.01 - 25 weight section (D) The ambient atmosphere amelioration agent which becomes the evaporation functionality propolis solid constituent characterized by the content of a component being 0.1 - 50

weight section and a list from this evaporation functionality propolis solid constituent is offered.

[0011] Moreover, the above-mentioned evaporation functionality propolis solid constituent The solution which will make the mixture of the water soluble solvent which can carry out hydrogen bond to (B) water independent or water, and water come to carry out the micell dissolution of the (C) surfactant if the approach of this invention is followed, (A) Mixed contact of a propolis original lump and/or its extract residue can be carried out, it can consider as a distributed condition, subsequently to this (D) hydrophilic-property high molecular compound can be added, and it can manufacture by carrying out homogeneity mixing.

[0012]

[Embodiment of the Invention] In this invention, a propolis original lump may be used as a (A) component, and the residue obtained by carrying out extract processing of this propolis original lump by various approaches may be used, and both a propolis original lump and extract residue may be mixed and used. It is not restricted especially as a propolis original lump, but you may be the thing of what kind of the origin, for example, all can use the product from Brazil, the product from the U.S., the product from Germany, the China acid, etc.

[0013] Moreover, there is especially no limit as extract residue, and the residue conventionally obtained by carrying out extract processing of the propolis original lump by the well-known approach can be used. To the propolis residue and the pan which were obtained by carrying out extract processing, a propolis original lump, for example, using water, ethyl alcohol, a liquefied carbon dioxide, etc. as this extract processing residue After contacting the system and propolis original lump which come to carry out the micell dissolution of polyol and the fatty-acid-ester system surfactant to the solvent which has two or more OH radicals according to the approach indicated by JP,4-66544,B. The propolis residue to which these some surfactants are sticking can be mentioned to the front face which removed and obtained the fusibility component which is carrying out the homogeneity dissolution.

[0014] In this invention, the mixture of the water soluble solvent which can carry out hydrogen bond to water independence or water, and water is used as a (B) component. Here as an example of the water soluble solvent which can carry out hydrogen bond to water Methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, Ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, 1, 3-butylene glycol, a glycerol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, The ethylene glycol monopropyl ether, ethylene glycol mono-isopropyl ether, Ethylene glycol monobutyl ether, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the diethylene-glycol monopropyl ether, Diethylene-glycol mono-isopropyl ether, the diethylene-glycol monobutyl ether, Propylene glycol monomethyl ether, the propylene glycol monoethyl ether, The propylene glycol monopropyl ether, propylene glycol mono-isopropyl ether, The propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, The dipropylene glycol monoethyl ether, the dipropylene glycol monopropyl ether, Alcohols solvents, such as dipropylene glycol mono-isopropyl ether and the dipropylene glycol monobutyl ether, Ethylene glycol wood ether, ethylene glycol diethylether, Nitrogen containing solvents, such as ketones, such as ethers solvents, such as diethylene-glycol wood ether, diethylene-glycol diethylether, a furfural, and dioxane, an acetone, and a methyl ethyl ketone, and 2-methyl imidazolidinone, etc. are mentioned. These water soluble solvents may be used independently, and may mix and use two or more sorts.

[0015] As a surface active agent of the (C) component in this invention, there is especially no limit and both anionic the Nonion nature cationicity and an amphoteric surface active agent can use it. As an example of the above-mentioned anionic surfactant alkylaryl sulfonates Soap, such as sodium salt of various fatty acids, potassium salt, and a triethanolamine salt Sulfate hydrochloric acids, such as alkyl sulfate and an alkyl polyoxyalkylene ethereal sulfate salt, Alkyl phosphate, alkyl aryl phosphate, alkyl polyoxyalkylene ether phosphate, Phosphate and polystyrene sulfonate salts, such as alkyl aryl polyoxyalkylene ether phosphate, What is represented with polysoaps, such as polyacrylate, is mentioned, and these may be used independently and may be used combining two or more sorts.

[0016] As an example of the Nonion nature surface active agent, a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, A glycerine fatty acid ester, diglycerol fatty acid ester, triglycerol fatty acid ester, A tetra-glycerine fatty acid ester, a PENTA glycerine fatty acid ester, A hexa glycerine fatty acid ester, ethylene glycol fatty acid ester, Polyoxy-ethylene-glycol fatty acid ester, sucrose fatty acid ester, Fatty acid ester, such as JI (glycerol) borate fatty acid ester The alkyl polyoxyalkylene ether, the alkyl aryl polyoxyalkylene ether, Polyethers, such as polyoxy-ethylene-glycol polyoxypropylene glycol block polymer The third class-sized amines, such as N and N-JI (polyoxyalkylene) alkylamine, N and N, N', and N'-tetrapod (polyoxyalkylene) ethylenediamine, And what is represented with amides, such as a fatty-acid mono-ARUKI roll amide and a fatty-acid JIARUKI roll amide, is mentioned, and these may be used independently and may be used combining two or more sorts.

[0017] As an example of a cationic surfactant, what is represented with quaternary ammonium salt, such as tetra-alkyl ammonium salt, trialkyl (beta-hydroxyalkyl) ammonium salt, and JIARUKIRUJI (polyoxyalkylene) ammonium salt, is mentioned, and these may be used independently and may be used combining two or more sorts. Moreover, as an example of an amphoteric surface active agent, what is represented with phospholipid, such as betaines, such as a trialkyl betaine and an alkyl imidazoline betaine, and lecithin, etc. is mentioned, and these may be used independently and may be used combining two or more sorts. Especially in this invention, the macromolecule anionic surface active agent containing carboxylate is desirable as a surface active agent of this (C) component.

[0018] On the other hand, as an example of the hydrophilic high molecular compound of the (D) component in this invention, a carrageenan, an agar, the DIN powder, polyvinyl alcohol, polyacrylamide, polyethylene oxide, a carboxymethyl cellulose, guar gum, xanthan gum, bridge formation mold polyacrylate, bridge formation mold polyacrylamide, etc. are mentioned. Especially a carrageenan is suitable, although these may be used independently and you may use combining two or more sorts.

[0019] The evaporation functionality propolis solid constituent of this invention contains the aforementioned (A) component, the (B) component, the (C) component, and the (D) component, and the content of the surfactant of the (C) component is chosen in the range of per [ of the (A) component and the (B) component ] total quantity 100 weight section, and 0.01 - 25 weight section. If it is difficult for the content of this (C) component to carry out stable distribution of the (A) component under in the 0.01 weight section and it exceeds 25 weight sections, the evaporation functionality of the active principle of the propolis origin will be checked remarkably. (A) From fields, such as balance of the distributed stability of a component, and the evaporation functionality of an active principle, the content with this desirable (C) component is the range per [ of the (A) component and the (B) component ] total quantity 100 weight section, and of 0.1 - 5 weight section, and the range of 0.5 - 2 weight section is especially suitable for it.

[0020] On the other hand, the content of the hydrophilic high molecular compound of the (D) component is chosen in the range of per [ of the (A) component and the (B) component ] total quantity 100 weight section, and 0.1 - 50 weight section. If solidification of a constituent is difficult for the content of this (D) component in under the 0.1 weight section and it exceeds 50

weight sections, the evaporation functionality of the active principle of the propolis origin will be checked remarkably. If solidification of a constituent, the evaporation functionality of an active principle, etc. are taken into consideration, the content with this desirable (D) component is the range per [ of the (A) component and the (B) component ] total quantity 100 weight section, and of 0.5 - 10 weight section, and the range of 1 - 5 weight section is especially suitable for it.

[0021] Moreover, as for the content rate of the (A) component and the (B) component, it is desirable that it is in the range of 1:999-1:2 by the weight ratio. (A) When there are few components than the above-mentioned range, there is a possibility that there may be too few amounts of the active principle of the propolis origin, and the purpose of this invention may not be reached, and if [ than the above-mentioned range ] more, the inclination for the distributed stability of the (A) component to worsen will be seen. (A) The range of the more desirable content rate of a component and the (B) component is 1:99-1:4 in a weight ratio, and especially the range of 1:49-1:9 is suitable for it.

[0022] Next, the manufacture approach of the evaporation functionality propolis solid constituent of this invention is explained. In the approach of this invention, the surfactant which is the (C) component is added into the mixture of the water independent or water which is the (B) component first, and said water soluble solvent, the micell dissolution is carried out, and the propolis original lump which is the (A) component further, and/or its extract residue are added, or a propolis original lump and/or its extract residue are added to a surfactant and coincidence. In addition, although it is based also on the class and amount of the surfactant in case a surfactant uses what is adsorbed as a propolis original lump's extract residue, it may be necessary to add a surfactant as the above-mentioned (C) component.

[0023] Thus, after adding a propolis original lump and/or its extract residue, preferably, mixed contact is preferably carried out at the temperature of 15-100 degrees C, and 15-200 degrees C is especially made into a distributed condition. Subsequently, 0-200 degrees C of these dispersion liquid are preferably held in temperature of 0-100 degrees C especially preferably by remaining as it is, or cooling or heating, the hydrophilic high molecular compound which is the (D) component is added, homogeneity mixing is carried out, and standing is carried out to this. After discharging from equipment after carrying out standing within a manufacturing installation and considering as a solid constituent in that case, and discharging from equipment with a liquid condition, standing is taken and carried out to a container and it is good also as a solid constituent.

[0024] In addition, even if it adds a hydrophilic high molecular compound for the polyol and fatty-acid-ester system surfactant micell-sized liquid food only containing the propolis extract component based on the conventional technique (JP,4-66544,B) and carries out homogeneity mixing by the manufacture approach of the evaporation functionality propolis solid constituent of this invention, and the same approach, a uniform solid constituent is not obtain, and since the calculated separation liquid moreover emits an odor remarkably, a desirable thing is not obtain on manufacture and application.

[0025] Since the evaporation functionality propolis solid constituent of this invention will work according to the synergism of each component as an ambient atmosphere amelioration agent which brings about the scent of comfortable sensibility at the same time it severs a surrounding offensive odor if it is contacted to a gaseous phase in the condition as it is again or is used with equipments, such as a fan, it is very useful on the orthobiosis.

[0026] In the evaporation functionality propolis solid constituent of this invention, various additives, such as a coloring agent, antiseptics, an antioxidant, and an aromatic, can be added by request in the range in which the purpose of this invention is not spoiled.

[0027]

[Example] Next, although an example and an application explain this invention to a detail further, this invention is not limited at all by these examples.

[0028] The water 90 weight section, the glycerol 5 weight section, the tetra-glycerol monooleate 1 weight section, and the sodium polyacrylate 0.01 weight section of average degree of polymerization 5000 were taught to the direct-vent-system reactor equipped with example 1 agitator, a thermometer, and heating apparatus, under ordinary pressure, it stirred for 20 minutes at 40 degrees C, and the uniform solution was prepared. Subsequently, after having added the propolis original lump 5 weight section from Brazil, stirring and carrying out mixed contact at 30-40 degrees C into this solution and considering as a distributed condition, to 60 degrees C, the temperature up was carried out, homogeneity mixing was carried out, adding and stirring the carrageenan [product [ made from MRC Poly Saccharide ] and trade name:SOAGINA WX-560] 2.5 weight section to this, and it discharged from the reactor at 50-60 degrees C. Then, standing was carried out at 20 degrees C for 24 hours, and the blackish brown evaporation functionality propolis solid constituent was obtained.

[0029] This constituent was put into the up disconnection container, and the situation of the gestalt one day after standing and of 30 days after and a surface odor was observed at 20 degrees C. A result is shown in Table 1.

[0030] In the homogeneity solution which consists of the example of comparison 1 water 90 weight section, the glycerol 5 weight section, the tetra-glycerol monooleate 1 weight section, and the sodium polyacrylate 0.01 weight section of average degree of polymerization 5000 As opposed to the solution which made the propolis extract component (extracting solvent: what consists of 10 % of the weight [ of water ], 89 % of the weight [ of glycerols ], and 1 % of the weight of tetra-glycerol monooleate) 5 weight section contain furthermore After adding the same carrageenan 2.5 weight section as what was used in the example 1 and carrying out homogeneity mixing like an example 1, standing was carried out at 20 degrees C for 24 hours, and the solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 1.

[0031]

[Table 1]

表1

	20℃, 1日静置後		20℃, 30日静置後	
	形態	表面臭気	形態	表面臭気
実施例1	均一固形	さわやかな香り	均一固形	さわやかな香り
比較例1	表面に液状物分布	刺激性臭気あり	上部に液相、下部に固相と分離	刺激性臭気強い

[0032] In the constituent of an example 1, Table 1 shows that evaporation functionality is acting so that each constituent may be compound-sized correctly and may make a good ambient atmosphere.

[0033] After teaching the water 90 weight section and the polyacrylic acid potassium 0.01 weight section of average degree of polymerization 3000 to the direct-vent-system reactor equipped with example 2 agitator, a thermometer, heating, and a cooling

system and performing stirring for 30 minutes at 15 degrees C, the propolis original lump 10 weight section from Brazil was added in this solution, and under the pressurization of 5kg/cm2G, mixed contact was carried out at 95-100 degrees C for 3 hours, and it considered as the distributed condition.

[0034] Subsequently, after lowering an internal temperature to 0 degree C, the whole quantity was moved to another open-end reactor, under stirring, the bridge formation mold sodium polyacrylate [Showa Denko K.K. make and trade name: BISUKO mate PX-112] 3 weight section was added to these dispersion liquid, homogeneity mixing was carried out for 10 minutes, and the brown evaporation functionality propolis solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 2.

[0035] The same bridge formation mold sodium polyacrylate 3 weight section as what was used in the example 2 to the solution which made the propolis extract component (extracting solvent: ethyl alcohol) 10 weight section contain further into the homogeneity solution which consists of the example of comparison 2 water 90 weight section and the polyacrylic acid potassium 0.01 weight section of average degree of polymerization 3000 was added, and the solid constituent was obtained like the example 2. About this constituent, it evaluated like the example 1. A result is shown in Table 2.

[0036]

[Table 2]

表 2

	20℃, 1日静置後		20℃, 30日静置後	
	形態	表面臭気	形態	表面臭気
実施例 2	均一・顆粒状固形	さわやかな香り	約30%分が蒸発して小さくなった顆粒	さわやかな香り
比較例 2	所々に液状物分布	刺激性臭気あり	表面に液体膜がでる	油臭が強くなる

[0037] In the constituent of an example 2, each constituent is compound-ized correctly and Table 2 shows that evaporation functionality is also acting favorably.

[0038] The evaporation functionality propolis solid constituent was manufactured like the example 1 or the example 2 using the (A) component of the class shown in three to example 8 Table 3 and 4, and an amount, the (B) component, the (C) component, and the (D) component. These constituents were put into the well-closed container, respectively, and the situation of the gestalt after standing and a surface odor was observed for 30 days at 20 degrees C. A result is shown in Table 5.

[0039]

[Table 3]

表 3

実施例	(A) 成分	(B) 成分	(C) 成分	(D) 成分	製造方法
3	ブラジル産 プロポリス原塊 7 重量部	水 8 0 重量部 エチルアルコール 1 0 重量部 ジエチレングリコール モノメチルエーテル 3 重量部	ポリ (10) オキシエチレンノニルフエニル エーテルリン酸アンモニウム 1 重量部 N, N-ジ [ポリ (5) オキシエチレン] ラウリルアミン 1 重量部 平均重合度 2 0 0 0 のステレン-マレイン 酸ナトリウム共重合体 0. 2 重量部	カラギーナン (MRCポリ サッカライド社製ソアギーナ WX-560) 4 重量部 グア-ガム 1 重量部	実施例 1 の 製造方法に 準じる
4	ブラジル産 プロポリス原塊 4 重量部	水 9 0 重量部 ジオキサン 3 重量部 エチレングリコールジ メチルエーテル 3 重量部	オレイン酸カリウム 0. 3 重量部 ポリ (8) オキシエチレンオクチル フェニルエーテル 1. 2 重量部 ラウリル硫酸ナトリウム 0. 5 重量部 平均重合度 2 0 0 0 のメタクリル酸 カリウム (9 : 1 モル比) 共重合体 0. 5 重量部	カラギーナン (MRCポリ サッカライド社製ソアギーナ MW-351) 5 重量部 キサンタンガム 0. 3 重量部 カルボキシメチルセルロース 0. 2 重量部	同 上
5	米国産 プロポリス原塊 1 0 重量部	水 8 4 重量部 1, 3-ブチレン グリコール 5 重量部 アセトン 1 重量部	平均分子量 2 0 0 0 のポリプロピレン グリコールの両側に平均分子量 2 0 0 0 のポリエチレングリコールをブロック ポリマー化させたもの 2 4 重量部 平均重合度 6 0 0 0 のアクリルアミド- アクリル酸ナトリウム (1 : 4 モル比) 共重合体 1 重量部	カラギーナン (MRCポリ サッカライド社製ソアギーナ MM-301) 3 重量部 デンプン 1 重量部 グア-ガム 2 重量部	同 上

[0040]

[Table 4]



表 4

実施例	(A) 成分	(B) 成分	(C) 成分	(D) 成分	製造方法
6	中国産 プロポリス原塊 1 重量部	水 98 重量部	平均重合度6000のポリアクリル酸 ナトリウム 0.01 重量部	カラギーナン (MRCポリリサッカ ライド社製ソアギーナMW-280) 1 重量部 平均重合度5000の70% ポリビニルアルコール 29 重量部 平均重合度2000のポリエチレン オキサライド 20 重量部	実施例1の 製造方法に 準じる
7	ブラジル産 プロポリス原塊 20 重量部	水 78 重量部 イソプロピルアルコール 1 重量部 フルフラール 0.5 重量部 2-メチルイミダゾリジ ノン 0.5 重量部	ジヘキサデシルジメチルアンモニウム クロリド 0.1 重量部 ドデシルジメチルベタイン 0.1 重量部 レンチン 0.2 重量部 平均重合度1000のポリアクリル 酸アンモニウム 0.6 重量部	カラギーナン (MRCポリリサッカ ライド社製ソアギーナMM-501) 0.05 重量部 精製寒天粉末 0.05 重量部	同 上
8	中国産 プロポリス原塊 5 重量部	水 90 重量部 メタノール 5 重量部	ポリ (10) オキシエチレン グリコールモノラウレート 0.8 重量部 平均重合度4000のアクリルアミド -アクリル酸ナトリウム (1:9モル 比) 共重合体 0.2 重量部	カラギーナン (MRCポリリサッカ ライド社製ソアギーナWX-560) 0.01 重量部 架橋型ポリアクリル酸ナトリウム (昭和電工 (株) 製ビスコメート PX-112) 0.02 重量部 架橋型ポリアクリル酸ナトリウム- ポリアクリルアミド共重合体 (台湾 製マジッククリスタル800) 0.07 重量部	実施例2の 製造方法に 準じる

[0041]

[Table 5]

表 5

		20℃, 30日静置後	
		形 態	表面臭気
実 施 例	3	均一固形	さわやかな香り
	4	"	"
	5	"	"
	6	"	"
	7	"	"

[0042] Table 5 shows that the constituent of examples 3-8 has the outstanding engine performance.

[0043] After carrying out heating contact of the solution which consists of the example 9 sorbitan-monolaurate 1 weight section and the glycerol 100 weight section, and the Brazil acid propolis original lump 5 weight section at 60-70 degrees C for 1 hour, solvent extraction was carried out, micell-izing and the part which is carrying out the homogeneity dissolution were removed, and propolis extract residue was obtained.

[0044] After teaching the above-mentioned propolis extract residue (composite which consists of the propolis residue 6 weight section, the sorbitan monolaurate 0.04 weight section adhering to it, and the glycerol 4 weight section) to the open-end reactor equipped with an agitator, a thermometer, heating, and a cooling system, the water 85 weight section, the ethyl alcohol 5 weight section, and the sodium polyacrylate 0.01 weight section of average degree of polymerization 5000 were taught, and homogeneity mixing was carried out at 20 degrees C under ordinary pressure. Subsequently, after adding the carrageenan [product [ made from MRC Poly Saccharide ] and trade name:SOAGINA WX-560] 5 weight section to this and carrying out a temperature up to 60 degrees C, heating gradually, it discharged from the reactor at this temperature, standing was carried out at 20 degrees C for 24 hours, and the blackish brown evaporation functionality propolis solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 6.

[0045] After carrying out heating contact of the solution which consists of the example 10 tetra-glycerol monooleate 1 weight section and the propylene glycol 100 weight section, and the propolis original lump 5 weight section from China for 30 minutes at 60-70 degrees C, the part which is extracted micell-ization and is carrying out the homogeneity dissolution was removed, and propolis extract residue was obtained.

[0046] After teaching the above-mentioned propolis extract residue (composite which consists of the propolis residue 9 weight section, the tetra-glycerol monooleate 0.01 weight section adhering to it, and the propylene glycol 1 weight section) to the open-end reactor equipped with the agitator, the water 90 weight section was taught, and homogeneity mixing was stirred and carried out at 20 degrees C. Subsequently, the bridge formation mold sodium polyacrylate [Showa Denko K.K. make and trade name:BISUKO mate PX-112] 3 weight section was added to this, it mixed to homogeneity for 15 minutes, and the brown evaporation functionality propolis solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 6.

[0047]

[Table 6]

表 6

		20℃, 1日静置後		20℃, 30日静置後	
		形 態	表面臭気	形 態	表面臭気
実施例 9		均一固形	さわやかな香り	約20%分が蒸発して小さくなった均一固形	さわやかな香り
実施例 10		均一顆粒状固形	さわやかな香り	約30%分が蒸発して小さくなった顆粒	さわやかな香り

[0048] Table 6 shows that each constituent is right, and the constituent of examples 9 and 10 is compound-ized, and evaporation functionality is also acting certainly.

[0049] 120 20-60-year-old man and woman who drive application 1 automobile were chosen at random, and it considered as the candidate. The up disconnection cylinder container with a diameter [ of 6cm ] and a height of 6cm was filled up with 100g of each solid constituent obtained in the evaporation functionality propolis solid constituent and the examples 1 and 2 of a comparison which were acquired in the examples 1-10, it was fixed to the front seat mid gear of 1800-3000 cc displacement passenger car for a trial, and it carried out according to the point which shows the odor feeling in that case, and the panel test about the temper at the time of operation below. A result is shown in Table 7.

[0050] (1) After considering as the condition of having made it stopping in the 24 hour uninhabited with room temperature conditions state, the door by the side of a front seat is opened, and I made ten candidates smell an odor in the car, and had them to fix a class product to the passenger car for a trial it was made to run 1 daily mean more than over odor feeling 1 year for 3 hours, to shut all of a door and an aperture and answer about one sort of constituents.

[0051] (2) Fix a class product to the passenger car for a trial it was made to run 1 daily mean more than over the temper 1 year at the time of operation for 3 hours. After considering as the condition of having shut all of a door and an aperture and having stopped them in the state of the room temperature for 24 hours in the uninhabited state, I had ten candidates ride for 3 hours (however, it considered as transit for 15-minute transit [ per hour ] -> 30 minutes for halt -> 15 minutes per hour), and had you answer about the passenger car for a trial furnished with one sort of constituents.

[0052]

[Table 7]

表7

試料	臭気感覚 ※1	運転時の気分 ※2
実施例 1	A	◎
実施例 2	A	◎
実施例 3	A	◎
実施例 4	A	◎
実施例 5	A	◎
実施例 6	A	◎
実施例 7	A	◎
実施例 8	A	◎
実施例 9	A	◎
実施例 10	A	◎
比較例 1	D	△
比較例 2	D	△

## [0053] [Notes]

\*\*1 The valuation basis of odor feeling is as follows.

That it is being supposed that the smell in the car which had all A...10 examiners conventionally was lost, and was become a desirable smell.

That which 1-3 persons sense that is not different from the former, and 9-7 persons are presupposing was become a smell with desirable others among the B10 person examiner.

That it is being supposed that was become the odor which 4-6 persons sensed that it was not different from the former among C...10 examiners, and changed other 6-4 persons.

Those who 7-9 persons have a too strong odor, sense that are not desirable, and sense are not it, either among D...10 examiners are three or less persons' things.

[0054] \*\*2 The valuation basis of the temper at the time of operation is as follows.

O ... That it was presupposed that all ten examiners can operate with a temper more sufficient than before.

O ... That it is being supposed that 7-9 persons can operate now with a temper more sufficient than before among ten examiners.

\*\* ... Those who presupposed that it can operate with a temper more sufficient than before among ten examiners are six or less persons' things.

The evaporation functionality propolis solid constituent of this invention becomes good [ odor feeling and the temper at the time of operation ], and it turns out that it is what is very excellent as an ambient atmosphere amelioration agent in a passenger car so that clearly from Table 7.

▷[0055] an application 2 — 120 15-65-year-old man and woman who have the symptom of chronic rhinitis were chosen at random, and it considered as the candidate. The cylinder container with a diameter [ of 7.2cm ] and a height of 8.8cm which opened \*\*\*\* with a diameter of 2.2cm in the center of the upper part is filled up with 300g of each solid constituent obtained in the evaporation functionality propolis solid constituent and the examples 1 and 2 of a comparison which were acquired in the examples 1-10. Attach in the blower (Taiwan AIR FREASURE, 8.5cmx9cmx24cm) having a motor and a sirocco fan, and it fixes to the location of 50cm from a head at the time of sleeping of an examiner. The odor feeling in the condition of having operated the blower for 1 daily-mean 8 hours, and the panel test about the temper in the case of breathing were carried out according to the point shown below. A result is shown in Table 8.

[0056] (1) Fell asleep to ten candidates about one sort of constituents, and I made the odor near a head smell in front, and had you answer after [ of the 1st day ] 15 minutes which operated the blower furnished with an odor feeling class product.

(2) I had ten candidates breathe deeply and had you answer about one sort of constituents at the \*\*\*\* time 30 days after operating 8 hours of Nighttime 1 daily means at a time the blower furnished with the temper class product in the case of breathing.

[0057]

[Table 8]

表 8

試 料	臭気感覚 ※1	運転時の気分 ※2
実施例 1	A	◎
実施例 2	A	◎
実施例 3	A	◎
実施例 4	A	◎
実施例 5	A	◎
実施例 6	A	◎
実施例 7	A	◎
実施例 8	A	◎
実施例 9	A	◎
実施例 10	A	◎
比較例 1	D	△
比較例 2	D	△

## [0058] [Notes]

\*\*1 The valuation basis of odor feeling is as follows.

That it is being supposed that all A...10 examiners are desirable smells.

That which 1-3 persons of an odor are too strong, senses that is not desirable, and 9-7 persons are presupposing was become a smell with desirable others among B...10 examiners.

That it is also being supposed that 4-6 persons have a too strong odor, and sense that it is not desirable among C...10 examiners, and other 6-4 persons are not them.

Those whom 7-9 persons are presupposing an odor is too strong, and it senses that it is not desirable, and is not it, either among D...10 examiners are three or less persons' things.

[0059] \*\*2 The valuation basis of the temper in the case of breathing is as follows.

O ... That it is being supposed that all ten examiners can breathe now with a temper more sufficient than blower installation-and actuation before.

O ... That it is being supposed that 7-9 persons can breathe now with a temper more sufficient than blower installation-and actuation before among ten examiners.

\*\* ... Those who sense that it can breathe now with a temper more sufficient than blower installation-and actuation before among ten examiners are six or less persons' things.

Odor feeling and the temper of sensibility in the case of breathing are [ the evaporation functionality propolis solid constituent of this invention ] good, and it turns out that it is what is very excellent as an indoor ambient atmosphere amelioration agent so that clearly from Table 8.

[0060]

[Effect of the Invention] The evaporation functionality propolis solid constituent of this invention solidifies the homogeneity dispersion liquid which were made to carry out mixed contact with the drainage system micellar solution of a surfactant, and were obtained in the form of the extract residue with the original lump which does not make the active principle and support component of propolis separate with a hydrophilic high molecular compound, turns into a solid stable in presentation, an evaporation component transpires regularly and continuously, and it gives good odor feeling, and is useful as an ambient atmosphere amelioration agent etc.

[0061] Therefore, it also makes it possible to apply as a subsistence store which newly installs to an environment a role of the natural antibacterial substance and natural health promotion matter which propolis has only not only in the application as conventional drink health food by carrying out this invention.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to an evaporation functionality propolis solid constituent, its manufacture approach, and an ambient atmosphere amelioration agent. In more detail, this invention has evaporation functionality, and is stabilized, gives good odor feeling, and relates to the ambient atmosphere amelioration agent which consists of the approach and the above-mentioned propolis solid constituent which manufacture efficiently a propolis solid constituent useful as an ambient atmosphere amelioration agent etc., and this thing.

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## PRIOR ART

[Description of the Prior Art] Conventionally, the propolis known as a natural antibacterial substance, the natural health promotion matter, etc. is the composite of the secondary metabolite represented by the flavonoids which phanerogamaes collected by Arthropoda, such as a honeybee, such as poplar and a pine, produce, and phenols, and the low matter and salivation object which Arthropoda produces. When making this thing edible, if it remains as it is, since it is too much hard and unsuitable to edible, what used as solution food with the extraction method using ethyl alcohol or a liquefied carbon dioxide, or was usually extracted is mixed with water-soluble polysaccharide, and edible is presented as a solid food article which is easy to disassemble with saliva easily.

[0003] However, the above-mentioned extraction method makes the origin the indiscriminate extraction method which uses a good solvent, and since even both the low matter originally considered not to participate in antibacterial ability or a health promotion function is extracted, nonaqueous solubility is emphasized including the component which is not useful, an extract will be in the condition of being hard to eat, and, moreover, it will become unstable with a drainage system solution. Therefore, even when using as a subsistence store generally, there was a problem that it did not escape that an application is restricted remarkably.

[0004] Although the approach of building the product which extracts only water-soluble materials and is easy to eat is also devised by on the other hand contacting a propolis original lump and water in the food field, this approach cannot take out an oil solubility active principle, and there are also few sampling volumes of water-soluble materials, and it cannot be said as the approach which may be satisfied efficiently.

[0005] Under such circumstances, this invention person invented the propolis food constituent using the hydrophilic solution micell of polyol and a fatty-acid-ester system surfactant by the so-called micell extraction method, and its manufacture approach previously as the approach of satisfying both the engine-performance side on a component extract, and the ease of eating (JP,4-66544,B). While the propolis food which is easy to eat is obtained according to this technique, the liquid propolis food which does not make the low matter which is not useful include can be manufactured by the sorting alternative extractor style, taking out the active principle of water-soluble and oil solubility.

[0006] However, by the system, the peculiar odor was emphasized and there was difficulty as a common subsistence store with which contact in the open air serves as a requirement.

[0007] On the other hand, although there are an American product which confined the propolis component extract into the maltose of a low-molecular solid-state, a tablet product infiltrated into the cellulose of nonaqueous solubility as a propolis solid constituent. From the above-mentioned liquid propolis food product, these are not built only with the advantage of being easy to bring, and did not have evaporation functionality, and the odor also suffered misfortune, and the expansion to fields other than food was unsuitable only at it.

[Translation done.]

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EFFECT OF THE INVENTION

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[Effect of the Invention] The evaporation functionality propolis solid constituent of this invention solidifies the homogeneity dispersion liquid which were made to carry out mixed contact with the drainage system micellar solution of a surfactant, and were obtained in the form of the extract residue with the original lump which does not make the active principle and support component of propolis separate with a hydrophilic high molecular compound, turns into a solid stable in presentation, an evaporation component transpires regularly and continuously, and it gives good odor feeling, and is useful as an ambient atmosphere amelioration agent etc.

[0061] Therefore, it also makes it possible to apply as a subsistence store which newly installs to an environment a role of the natural antibacterial substance and natural health promotion matter which propolis has only not only in the application as conventional drink health food by carrying out this invention.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation, it has evaporation functionality, and it is stabilized, gives good odor feeling, and aims at offering the ambient atmosphere amelioration agent which consists of the approach and the above-mentioned propolis solid constituent which manufacture efficiently a propolis solid constituent useful as an ambient atmosphere amelioration agent etc., and this thing.

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## MEANS

[Means for Solving the Problem] In order that this invention person may attain said purpose, as a result of repeating research wholeheartedly, a propolis original lump and/or its extract residue, The mixture, the surfactant, and the hydrophilic high molecular compound of water or water, and a specific water soluble solvent The solid constituent contained at a predetermined rate, respectively the active principle of the propolis origin which are a natural antibacterial substance and the health promotion matter Have the evaporation functionality of transpiring a minute amount [ every ] continuation target, and it is stabilized, give good odor feeling, and useful as an ambient atmosphere amelioration agent etc., and this propolis solid constituent In the solution which makes the mixture of water or water, and a specific water soluble solvent come to carry out the micell dissolution of the surfactant, carry out homogeneity distribution of a propolis original lump and/or its extract residue, add a hydrophilic high molecular compound to this, and by carrying out homogeneity mixing Based on a header and this knowledge, it came to complete this invention for the ability to manufacture efficiently.

[0010] This invention Namely, a (A) propolis original lump and/or its extract residue, (B) Mixture of the water soluble solvent which can carry out hydrogen bond to a water independent or water, and water, (C) A surfactant and (D) hydrophilic-property high molecular compound are contained. The content of per [ of the (A) component and the (B) component ] total quantity 100 weight section and the (C) component in 0.01 - 25 weight section (D) The ambient atmosphere amelioration agent which becomes the evaporation functionality propolis solid constituent characterized by the content of a component being 0.1 - 50 weight section and a list from this evaporation functionality propolis solid constituent is offered.

[0011] Moreover, the above-mentioned evaporation functionality propolis solid constituent The solution which will make the mixture of the water soluble solvent which can carry out hydrogen bond to (B) water independent or water, and water come to carry out the micell dissolution of the (C) surfactant if the approach of this invention is followed, (A) Mixed contact of a propolis original lump and/or its extract residue can be carried out, it can consider as a distributed condition, subsequently to this (D) hydrophilic-property high molecular compound can be added, and it can manufacture by carrying out homogeneity mixing.

[0012]

[Embodiment of the Invention] In this invention, a propolis original lump may be used as a (A) component, and the residue obtained by carrying out extract processing of this propolis original lump by various approaches may be used, and both a propolis original lump and extract residue may be mixed and used. It is not restricted especially as a propolis original lump, but you may be the thing of what kind of the origin, for example, all can use the product from Brazil, the product from the U.S., the product from Germany, the China acid, etc.

[0013] Moreover, there is especially no limit as extract residue, and the residue conventionally obtained by carrying out extract processing of the propolis original lump by the well-known approach can be used. To the propolis residue and the pan which were obtained by carrying out extract processing, a propolis original lump, for example, using water, ethyl alcohol, a liquefied carbon dioxide, etc. as this extract processing residue After contacting the system and propolis original lump which come to carry out the micell dissolution of polyol and the fatty-acid-ester system surfactant to the solvent which has two or more OH radicals according to the approach indicated by JP,4-66544,B. The propolis residue to which these some surfactants are sticking can be mentioned to the front face which removed and obtained the fusibility component which is carrying out the homogeneity dissolution.

[0014] In this invention, the mixture of the water soluble solvent which can carry out hydrogen bond to water independence or water, and water is used as a (B) component. Here as an example of the water soluble solvent which can carry out hydrogen bond to water Methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, Ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, 1, 3-butylene glycol, a glycerol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, The ethylene glycol monopropyl ether, ethylene glycol mono-isopropyl ether, Ethylene glycol monobutyl ether, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the diethylene-glycol monopropyl ether, Diethylene-glycol mono-isopropyl ether, the diethylene-glycol monobutyl ether, Propylene glycol monomethyl ether, the propylene glycol monoethyl ether, The propylene glycol monopropyl ether, propylene glycol mono-isopropyl ether, The propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, The dipropylene glycol monoethyl ether, the dipropylene glycol monopropyl ether, Alcohols solvents, such as dipropylene glycol mono-isopropyl ether and the dipropylene glycol monobutyl ether, Ethylene glycol wood ether, ethylene glycol diethylether, Nitrogen containing solvents, such as ketones, such as ethers solvents, such as diethylene-glycol wood ether, diethylene-glycol diethylether, a furfural, and dioxane, an acetone, and a methyl ethyl ketone, and 2-methyl imidazolidinone, etc. are mentioned. These water soluble solvents may be used independently, and may mix and use two or more sorts.

[0015] As a surface active agent of the (C) component in this invention, there is especially no limit and both anionic the Nonion nature cationicity and an amphoteric surface active agent can use it. As an example of the above-mentioned anionic surfactant alkylaryl sulfonates Soap, such as sodium salt of various fatty acids, potassium salt, and a triethanolamine salt Sulfate hydrochloric acids, such as alkyl sulfate and an alkyl polyoxyalkylene ethereal sulfate salt, Alkyl phosphate, alkyl aryl phosphate, alkyl polyoxyalkylene ether phosphate, Phosphate and polystyrene sulfonate salts, such as alkyl aryl polyoxyalkylene ether phosphate, What is represented with polysoaps, such as polyacrylate, is mentioned, and these may be used independently and may be used combining two or more sorts.

[0016] As an example of the Nonion nature surface active agent, a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, A glycerine fatty acid ester, diglycerol fatty acid ester, triglycerol fatty acid ester, A tetra-glycerine fatty acid ester, a PENTA glycerine fatty acid ester, A hexa glycerine fatty acid ester, ethylene glycol fatty acid ester, Polyoxy-ethylene-glycol

fatty acid ester, sucrose fatty acid ester, Fatty acid ester, such as JI (glycerol) borate fatty acid ester The alkyl polyoxyalkylene ether, the alkyl aryl polyoxyalkylene ether, Polyethers, such as polyoxy-ethylene-glycol polyoxypropylene glycol block polymer The third class-ized amines, such as N and N-JI (polyoxyalkylene) alkylamine, N and N, N', and N'-tetrapod (polyoxyalkylene) ethylenediamine, And what is represented with amides, such as a fatty-acid mono-ARUKI roll amide and a fatty-acid JIARUKI roll amide, is mentioned, and these may be used independently and may be used combining two or more sorts.

[0017] As an example of a cationic surfactant, what is represented with quarternary ammonium salt, such as tetra-alkyl ammonium salt, trialkyl (beta-hydroxyalkyl) ammonium salt, and JIARUKIRUJI (polyoxyalkylene) ammonium salt, is mentioned, and these may be used independently and may be used combining two or more sorts. Moreover, as an example of an amphoteric surface active agent, what is represented with phospholipid, such as betaines, such as a trialkyl betaine and an alkyl imidazoline betaine, and lecithin, etc. is mentioned, and these may be used independently and may be used combining two or more sorts. Especially in this invention, the macromolecule anionic surface active agent containing carboxylate is desirable as a surface active agent of this (C) component.

[0018] On the other hand, as an example of the hydrophilic high molecular compound of the (D) component in this invention, a carrageenan, an agar, the DIN powder, polyvinyl alcohol, polyacrylamide, polyethylene oxide, a carboxymethyl cellulose, guar gum, xanthan gum, bridge formation mold polyacrylate, bridge formation mold polyacrylamide, etc. are mentioned. Especially a carrageenan is suitable, although these may be used independently and you may use combining two or more sorts.

[0019] The evaporation functionality propolis solid constituent of this invention contains the aforementioned (A) component, the (B) component, the (C) component, and the (D) component, and the content of the surfactant of the (C) component is chosen in the range of per [ of the (A) component and the (B) component ] total quantity 100 weight section, and 0.01 - 25 weight section. If it is difficult for the content of this (C) component to carry out stable distribution of the (A) component under in the 0.01 weight section and it exceeds 25 weight sections, the evaporation functionality of the active principle of the propolis origin will be checked remarkably. (A) From fields, such as balance of the distributed stability of a component, and the evaporation functionality of an active principle, the content with this desirable (C) component is the range per [ of the (A) component and the (B) component ] total quantity 100 weight section, and of 0.1 - 5 weight section, and the range of 0.5 - 2 weight section is especially suitable for it.

[0020] On the other hand, the content of the hydrophilic high molecular compound of the (D) component is chosen in the range of per [ of the (A) component and the (B) component ] total quantity 100 weight section, and 0.1 - 50 weight section. If solidification of a constituent is difficult for the content of this (D) component in under the 0.1 weight section and it exceeds 50 weight sections, the evaporation functionality of the active principle of the propolis origin will be checked remarkably. If solidification of a constituent, the evaporation functionality of an active principle, etc. are taken into consideration, the content with this desirable (D) component is the range per [ of the (A) component and the (B) component ] total quantity 100 weight section, and of 0.5 - 10 weight section, and the range of 1 - 5 weight section is especially suitable for it.

[0021] Moreover, as for the content rate of the (A) component and the (B) component, it is desirable that it is in the range of 1:999-1:2 by the weight ratio. (A) When there are few components than the above-mentioned range, there is a possibility that there may be too few amounts of the active principle of the propolis origin, and the purpose of this invention may not be reached, and if [ than the above-mentioned range ] more, the inclination for the distributed stability of the (A) component to worsen will be seen. (A) The range of the more desirable content rate of a component and the (B) component is 1:99-1:4 in a weight ratio, and especially the range of 1:49-1:9 is suitable for it.

[0022] Next, the manufacture approach of the evaporation functionality propolis solid constituent of this invention is explained. In the approach of this invention, the surfactant which is the (C) component is added into the mixture of the water independent or water which is the (B) component first, and said water soluble solvent, the micell dissolution is carried out, and the propolis original lump which is the (A) component further, and/or its extract residue are added, or a propolis original lump and/or its extract residue are added to a surfactant and coincidence. In addition, although it is based also on the class and amount of the surfactant in case a surfactant uses what is adsorbed as a propolis original lump's extract residue, it may be necessary to add a surfactant as the above-mentioned (C) component.

[0023] Thus, after adding a propolis original lump and/or its extract residue, preferably, mixed contact is preferably carried out at the temperature of 15-100 degrees C, and 15-200 degrees C is especially made into a distributed condition. Subsequently, 0-200 degrees C of these dispersion liquid are preferably held in temperature of 0-100 degrees C especially preferably by remaining as it is, or cooling or heating, the hydrophilic high molecular compound which is the (D) component is added, homogeneity mixing is carried out, and standing is carried out to this. After discharging from equipment after carrying out standing within a manufacturing installation and considering as a solid constituent in that case, and discharging from equipment with a liquid condition, standing is taken and carried out to a container and it is good also as a solid constituent.

[0024] In addition, even if it adds a hydrophilic high molecular compound for the polyol and fatty-acid-ester system surfactant micell-ized liquid food only containing the propolis extract component based on the conventional technique (JP,4-66544,B) and carries out homogeneity mixing by the manufacture approach of the evaporation functionality propolis solid constituent of this invention, and the same approach, a uniform solid constituent is not obtain, and since the calculated separation liquid moreover emits an odor remarkably, a desirable thing is not obtain on manufacture and application.

[0025] Since the evaporation functionality propolis solid constituent of this invention will work according to the synergism of each component as an ambient atmosphere amelioration agent which brings about the scent of comfortable sensibility at the same time it severs a surrounding offensive odor if it is contacted to a gaseous phase in the condition as it is again or is used with equipments, such as a fan, it is very useful on the orthobiosis.

[0026] In the evaporation functionality propolis solid constituent of this invention, various additives, such as a coloring agent, antiseptics, an antioxidant, and an aromatic, can be added by request in the range in which the purpose of this invention is not spoiled.

[Translation done.]

## \* NOTICES \*

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## EXAMPLE

[Example] Next, although an example and an application explain this invention to a detail further, this invention is not limited at all by these examples.

[0028] The water 90 weight section, the glycerol 5 weight section, the tetra-glycerol monooleate 1 weight section, and the sodium polyacrylate 0.01 weight section of average degree of polymerization 5000 were taught to the direct-vent-system reactor equipped with example 1 agitator, a thermometer, and heating apparatus, under ordinary pressure, it stirred for 20 minutes at 40 degrees C, and the uniform solution was prepared. Subsequently, after having added the propolis original lump 5 weight section from Brazil, stirring and carrying out mixed contact at 30-40 degrees C into this solution and considering as a distributed condition, to 60 degrees C, the temperature up was carried out, homogeneity mixing was carried out, adding and stirring the carrageenan [product [ made from MRC Poly Saccharide ] and trade name:SOAGINA WX-560] 2.5 weight section to this, and it discharged from the reactor at 50-60 degrees C. Then, standing was carried out at 20 degrees C for 24 hours, and the blackish brown evaporation functionality propolis solid constituent was obtained.

[0029] This constituent was put into the up disconnection container, and the situation of the gestalt one day after standing and of 30 days after and a surface odor was observed at 20 degrees C. A result is shown in Table 1.

[0030] In the homogeneity solution which consists of the example of comparison 1 water 90 weight section, the glycerol 5 weight section, the tetra-glycerol monooleate 1 weight section, and the sodium polyacrylate 0.01 weight section of average degree of polymerization 5000 As opposed to the solution which made the propolis extract component (extracting solvent: what consists of 10 % of the weight [ of water ], 89 % of the weight [ of glycerols ], and 1 % of the weight of tetra-glycerol monooleate) 5 weight section contain furthermore After adding the same carrageenan 2.5 weight section as what was used in the example 1 and carrying out homogeneity mixing like an example 1, standing was carried out at 20 degrees C for 24 hours, and the solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 1.

[0031]

[Table 1]

表 1

	20℃, 1日静置後		20℃, 30日静置後	
	形態	表面臭気	形態	表面臭気
実施例 1	均一固形	さわやかな香り	均一固形	さわやかな香り
比較例 1	表面に液状物分布	刺激性臭気あり	上部に液相、下部に固相と分離	刺激性臭気強い

[0032] In the constituent of an example 1, Table 1 shows that evaporation functionality is acting so that each constituent may be compound-sized correctly and may make a good ambient atmosphere.

[0033] After teaching the water 90 weight section and the polyacrylic acid potassium 0.01 weight section of average degree of polymerization 3000 to the direct-vent-system reactor equipped with example 2 agitator, a thermometer, heating, and a cooling system and performing stirring for 30 minutes at 15 degrees C, the propolis original lump 10 weight section from Brazil was added in this solution, and under the pressurization of 5kg/cm2G, mixed contact was carried out at 95-100 degrees C for 3 hours, and it considered as the distributed condition.

[0034] Subsequently, after lowering an internal temperature to 0 degree C, the whole quantity was moved to another open-end reactor, under stirring, the bridge formation mold sodium polyacrylate [Showa Denko K.K. make and trade name:BISUKO mate PX-112] 3 weight section was added to these dispersion liquid, homogeneity mixing was carried out for 10 minutes, and the brown evaporation functionality propolis solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 2.

[0035] The same bridge formation mold sodium polyacrylate 3 weight section as what was used in the example 2 to the solution which made the propolis extract component (extracting solvent: ethyl alcohol) 10 weight section contain further into the homogeneity solution which consists of the example of comparison 2 water 90 weight section and the polyacrylic acid potassium 0.01 weight section of average degree of polymerization 3000 was added, and the solid constituent was obtained like the example 2. About this constituent, it evaluated like the example 1. A result is shown in Table 2.

[0036]

[Table 2]

表 2

	20℃, 1日静置後		20℃, 30日静置後	
	形 態	表面臭気	形 態	表面臭気
実施例 2	均一・顆粒状固形	さわやかな香り	約30%分が蒸発して小さくなった顆粒	さわやかな香り
比較例 2	所々に液状物分布	刺激性臭気あり	表面に液体膜がでる	油臭が強くなる

[0037] In the constituent of an example 2, each constituent is compound-ized correctly and Table 2 shows that evaporation functionality is also acting favorably.

[0038] The evaporation functionality propolis solid constituent was manufactured like the example 1 or the example 2 using the (A) component of the class shown in three to example 8 Table 3 and 4, and an amount, the (B) component, the (C) component, and the (D) component. These constituents were put into the well-closed container, respectively, and the situation of the gestalt after standing and a surface odor was observed for 30 days at 20 degrees C. A result is shown in Table 5.

[0039]

[Table 3]

表 3

実施例	(A) 成分	(B) 成分	(C) 成分	(D) 成分	製造方法
3	ブラジル産 プロポリス原塊 7 重量部	水 エチルアルコール 10 重量部 ジエチレングリコール モノメチルエーテル 3 重量部	ポリ (10) オキシエチレンノニルフエニル エーテルリン酸アンモニウム 1 重量部 N, N-ジ [ポリ (5) オキシエチレン] ラウリルアミン 1 重量部 平均重合度 2000 のステレン-マレイン 酸ナトリウム共重合体 0.2 重量部 オレイン酸カリウム 0.3 重量部 ポリ (8) オキシエチレンオクテチル フェニルエーテル 1.2 重量部 ラウリル硫酸ナトリウム 0.5 重量部 平均重合度 2000 のメタクリル酸 カリウム (9:1 モル比) 共重合体 0.5 重量部	カラギーナン (MRC ポリ サッカライド社製ソアギーナ WX-560) 4 重量部 グアーガム 1 重量部	実施例 1 の 製造方法に 準じる
4	ブラジル産 プロポリス原塊 4 重量部	水 ジオキサン エチレングリコールジ メチルエーテル 3 重量部	平均分子量 2000 のポリプロピレン グリコールの両側に平均分子量 2000 のポリエチレングリコールをブロック ポリマー化させたもの 2.4 重量部 平均重合度 6000 のアクリルアミド- アクリル酸ナトリウム (1:4 モル比) 共重合体 1 重量部	カラギーナン (MRC ポリ サッカライド社製ソアギーナ MW-351) 5 重量部 キサンタンガム 0.3 重量部 カルボキシメチルセルロース 0.2 重量部	同 上
5	米国産 プロポリス原塊 10 重量部	水 1, 3-ブチレン グリコール アセトン 5 重量部 1 重量部		カラギーナン (MRC ポリ サッカライド社製ソアギーナ MM-301) 3 重量部 デンプン 1 重量部 グアーガム 2 重量部	同 上

[0040]  
[Table 4]

表 4

実施例	(A) 成分	(B) 成分	(C) 成分	(D) 成分	製造方法
6	中国産 プロポリス原塊 1 重量部	水 99 重量部	平均重合度 6000 のポリアクリル酸 ナトリウム 0.01 重量部	カラギーナン (MRC ポリサッカラ イド社製ソアギーナ MW-280) 1 重量部 平均重合度 5000 の 70% ポリビニルアルコール 29 重量部 平均重合度 2000 のポリエチレン オキサイド 20 重量部	実施例 1 の 製造方法に 準じる
7	ブラジル産 プロポリス原塊 20 重量部	水 78 重量部 イソプロピルアルコール 1 重量部 フルフラール 0.5 重量部 2-メチルイミダゾリジ ノン 0.5 重量部	ジヘキサデシルジメチルアンモニウム クロリド 0.1 重量部 ドデシルジメチルベタイン 0.1 重量部 レンチン 0.2 重量部 平均重合度 1000 のポリアクリル 酸アンモニウム 0.6 重量部	カラギーナン (MRC ポリサッカラ イド社製ソアギーナ MM-501) 0.05 重量部 精製寒天粉末 0.05 重量部	同 上
8	中国産 プロポリス原塊 5 重量部	水 90 重量部 メタノール 5 重量部	ポリ (10) オキシエチレン グリコールモノラウレート 0.8 重量部 平均重合度 4000 のアクリルアミド -アクリル酸ナトリウム (1:9 モル 比) 共重合体 0.2 重量部	カラギーナン (MRC ポリサッカラ イド社製ソアギーナ WX-560) 0.01 重量部 架橋型ポリアクリル酸ナトリウム (昭和電工 (株) 製ビスコメート PX-112) 0.02 重量部 架橋型ポリアクリル酸ナトリウム- ポリアクリルアミド共重合体 (台湾 製マジッククリスタル 800) 0.07 重量部	実施例 2 の 製造方法に 準じる

[0041]

[Table 5]

表5

		20℃, 30日静置後	
		形態	表面臭気
実施例	3	均一固形	さわやかな香り
	4	"	"
	5	"	"
	6	"	"
	7	"	"

[0042] Table 5 shows that the constituent of examples 3-8 has the outstanding engine performance.

[0043] After carrying out heating contact of the solution which consists of the example 9 sorbitan-monolaurate 1 weight section and the glycerol 100 weight section, and the Brazil acid propolis original lump 5 weight section at 60-70 degrees C for 1 hour, solvent extraction was carried out, micell-izing and the part which is carrying out the homogeneity dissolution were removed, and propolis extract residue was obtained.

[0044] After teaching the above-mentioned propolis extract residue (composite which consists of the propolis residue 6 weight section, the sorbitan monolaurate 0.04 weight section adhering to it, and the glycerol 4 weight section) to the open-end reactor equipped with an agitator, a thermometer, heating, and a cooling system, the water 85 weight section, the ethyl alcohol 5 weight section, and the sodium polyacrylate 0.01 weight section of average degree of polymerization 5000 were taught, and homogeneity mixing was carried out at 20 degrees C under ordinary pressure. Subsequently, after adding the carrageenan [product [ made from MRC Poly Saccharide ] and trade name:SOAGINA WX-560] 5 weight section to this and carrying out a temperature up to 60 degrees C, heating gradually, it discharged from the reactor at this temperature, standing was carried out at 20 degrees C for 24 hours, and the blackish brown evaporation functionality propolis solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 6.

[0045] After carrying out heating contact of the solution which consists of the example 10 tetra-glycerol monooleate 1 weight section and the propylene glycol 100 weight section, and the propolis original lump 5 weight section from China for 30 minutes at 60-70 degrees C, the part which is extracted micell-ization and is carrying out the homogeneity dissolution was removed, and propolis extract residue was obtained.

[0046] After teaching the above-mentioned propolis extract residue (composite which consists of the propolis residue 9 weight section, the tetra-glycerol monooleate 0.01 weight section adhering to it, and the propylene glycol 1 weight section) to the open-end reactor equipped with the agitator, the water 90 weight section was taught, and homogeneity mixing was stirred and carried out at 20 degrees C. Subsequently, the bridge formation mold sodium polyacrylate [Showa Denko K.K. make and trade name:BISUKO mate PX-112] 3 weight section was added to this, it mixed to homogeneity for 15 minutes, and the brown evaporation functionality propolis solid constituent was obtained. About this constituent, it evaluated like the example 1. A result is shown in Table 6.

[0047]

[Table 6]

表6

	20℃, 1日静置後		20℃, 30日静置後	
	形態	表面臭気	形態	表面臭気
実施例 9	均一固形	さわやかな香り	約20%分が蒸発して小さくなった均一固形	さわやかな香り
実施例 10	均一顆粒状固形	さわやかな香り	約30%分が蒸発して小さくなった顆粒	さわやかな香り

[0048] Table 6 shows that each constituent is right, and the constituent of examples 9 and 10 is compound-ized, and evaporation functionality is also acting certainly.

[0049] 120 20-60-year-old man and woman who drive application 1 automobile were chosen at random, and it considered as the candidate. The up disconnection cylinder container with a diameter [ of 6cm ] and a height of 6cm was filled up with 100g of each solid constituent obtained in the evaporation functionality propolis solid constituent and the examples 1 and 2 of a comparison which were acquired in the examples 1-10, it was fixed to the front seat mid gear of 1800-3000 cc displacement passenger car for a trial, and it carried out according to the point which shows the odor feeling in that case, and the panel test about the temper at the time of operation below. A result is shown in Table 7.

[0050] (1) After considering as the condition of having made it stopping in the 24 hour uninhabited with room temperature conditions state, the door by the side of a front seat is opened, and I made ten candidates smell an odor in the car, and had them to fix a class product to the passenger car for a trial it was made to run 1 daily mean more than over odor feeling 1 year for 3 hours, to shut all of a door and an aperture and answer about one sort of constituents.

[0051] (2) Fix a class product to the passenger car for a trial it was made to run 1 daily mean more than over the temper 1 year at the time of operation for 3 hours. After considering as the condition of having shut all of a door and an aperture and having stopped them in the state of the room temperature for 24 hours in the uninhabited state, I had ten candidates ride for 3 hours (however, it considered as transit for 15-minute transit [ per hour ] -> 30 minutes for halt -> 15 minutes per hour), and had you answer about the passenger car for a trial furnished with one sort of constituents.

[0052]

[Table 7]

表7

試料	臭気感覚 ※1	運転時の気分 ※2
実施例 1	A	◎
実施例 2	A	◎
実施例 3	A	◎
実施例 4	A	◎
実施例 5	A	◎
実施例 6	A	◎
実施例 7	A	◎
実施例 8	A	◎
実施例 9	A	◎
実施例 10	A	◎
比較例 1	D	△
比較例 2	D	△

## [0053] [Notes]

\*\*1 The valuation basis of odor feeling is as follows.

That it is being supposed that the smell in the car which had all A...10 examiners conventionally was lost, and was become a desirable smell.

That which 1-3 persons sense that is not different from the former, and 9-7 persons are presupposing was become a smell with desirable others among the B10 person examiner.

That it is being supposed that was become the odor which 4-6 persons sensed that it was not different from the former among C...10 examiners, and changed other 6-4 persons.

Those who 7-9 persons have a too strong odor, sense that are not desirable, and sense are not it, either among D...10 examiners are three or less persons' things.

[0054] \*\*2 The valuation basis of the temper at the time of operation is as follows.

O ... That it was presupposed that all ten examiners can operate with a temper more sufficient than before.

O ... That it is being supposed that 7-9 persons can operate now with a temper more sufficient than before among ten examiners.

\*\* ... Those who presupposed that it can operate with a temper more sufficient than before among ten examiners are six or less persons' things.

The evaporation functionality propolis solid constituent of this invention becomes good [ odor feeling and the temper at the time of operation ], and it turns out that it is what is very excellent as an ambient atmosphere amelioration agent in a passenger car so that clearly from Table 7.

[0055] an application 2 — 120 15-65-year-old man and woman who have the symptom of chronic rhinitis were chosen at random, and it considered as the candidate. The cylinder container with a diameter [ of 7.2cm ] and a height of 8.8cm which opened \*\*\*\* with a diameter of 2.2cm in the center of the upper part is filled up with 300g of each solid constituent obtained in the evaporation functionality propolis solid constituent and the examples 1 and 2 of a comparison which were acquired in the examples 1-10. Attach in the blower (Taiwan AIR FREASURE, 8.5cmx9cmx24cm) having a motor and a sirocco fan, and it fixes to the location of 50cm from a head at the time of sleeping of an examiner. The odor feeling in the condition of having operated the blower for 1 daily-mean 8 hours, and the panel test about the temper in the case of breathing were carried out according to the point shown below. A result is shown in Table 8.

[0056] (1) Fell asleep to ten candidates about one sort of constituents, and I made the odor near a head smell in front, and had you answer after [ of the 1st day ] 15 minutes which operated the blower furnished with an odor feeling class product.

(2) I had ten candidates breathe deeply and had you answer about one sort of constituents at the \*\*\*\* time 30 days after operating 8 hours of Nighttime 1 daily means at a time the blower furnished with the temper class product in the case of breathing.

[0057]

[Table 8]



表 8

試 料	臭気感覚 ※1	運転時の気分 ※2
実施例 1	A	◎
実施例 2	A	◎
実施例 3	A	◎
実施例 4	A	◎
実施例 5	A	◎
実施例 6	A	◎
実施例 7	A	◎
実施例 8	A	◎
実施例 9	A	◎
実施例 10	A	◎
比較例 1	D	△
比較例 2	D	△

## [0058] [Notes]

\*\*1 The valuation basis of odor feeling is as follows.

That it is being supposed that all A...10 examiners are desirable smells.

That which 1-3 persons of an odor are too strong, senses that is not desirable, and 9-7 persons are presupposing was become a smell with desirable others among B...10 examiners.

That it is also being supposed that 4-6 persons have a too strong odor, and sense that it is not desirable among C...10 examiners, and other 6-4 persons are not them.

Those whom 7-9 persons are presupposing an odor is too strong, and it senses that it is not desirable, and is not it, either among D...10 examiners are three or less persons' things.

[0059] \*\*2 The valuation basis of the temper in the case of breathing is as follows.

O ... That it is being supposed that all ten examiners can breathe now with a temper more sufficient than blower installation-and actuation before.

O ... That it is being supposed that 7-9 persons can breathe now with a temper more sufficient than blower installation-and actuation before among ten examiners.

\*\* ... Those who sense that it can breathe now with a temper more sufficient than blower installation-and actuation before among ten examiners are six or less persons' things.

Odor feeling and the temper of sensibility in the case of breathing are [ the evaporation functionality propolis solid constituent of this invention ] good, and it turns out that it is what is very excellent as an indoor ambient atmosphere amelioration agent so that clearly from Table 8.

[Translation done.]

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(54) 【発明の名称】 蒸発機能性プロポリス固形組成物、その製造方法及び雰囲気改良剤

## (57) 【要約】

【課題】 蒸発機能性を有し、かつ良好な臭気感覚を安定して与え、雰囲気改良剤などとして有用なプロポリス固形組成物を提供する。

【解決手段】 (A) プロポリス原塊やその抽出残渣、(B) 水または水および水と水素結合しうる水溶性溶剤の混合物、(C) 界面活性剤および(D) 親水性高分子化合物を含有し、かつ(A)成分と(B)成分との合計量 1 0 0 重量部当たり、(C)成分の含有量が 0. 0 1 ~ 2 5 重量部で、(D)成分の含有量が 0. 1 ~ 5 0 重量部である蒸発機能性プロポリス固形組成物。

## 【特許請求の範囲】

【請求項 1】 (A) プロポリス原塊および／またはその抽出残渣、(B) 水単独または水および水と水素結合しうる水溶性溶剤の混合物、(C) 界面活性剤および (D) 親水性高分子化合物を含有し、かつ (A) 成分と (B) 成分との合計量 100 重量部当たり、(C) 成分の含有量が 0.01～25 重量部で、(D) 成分の含有量が 0.1～50 重量部であることを特徴とする蒸発機能性プロポリス固形組成物。

【請求項 2】 (A) 成分と (B) 成分との含有割合が、重量比で 1:999～1:2 である請求項 1 に記載の蒸発機能性プロポリス固形組成物。

【請求項 3】 (C) 成分の界面活性剤がカルボン酸塩を含有する高分子アニオン性界面活性剤である請求項 1 または 2 に記載の蒸発機能性プロポリス固形組成物。

【請求項 4】 (D) 成分の親水性高分子化合物がカラギーナンである請求項 1、2 または 3 に記載の蒸発機能性プロポリス固形組成物。

【請求項 5】 (B) 水単独または水および水と水素結合しうる水溶性溶剤の混合物に (C) 界面活性剤をミセル溶解させてなる溶液と、(A) プロポリス原塊および／またはその抽出残渣とを混合接触させて、分散状態とし、次いで、これに (D) 親水性高分子化合物を添加して、均一混合することを特徴とする、請求項 1 または 2 に記載の蒸発機能性プロポリス固形組成物の製造方法。

【請求項 6】 (C) 成分の界面活性剤がカルボン酸塩を含有する高分子アニオン性界面活性剤である請求項 5 に記載の製造方法。

【請求項 7】 (D) 成分の親水性高分子化合物がカラギーナンである請求項 5 または 6 に記載の製造方法。

【請求項 8】 請求項 1～4 のいずれかに記載の蒸発機能性プロポリス固形組成物からなる雰囲気改良剤。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、蒸発機能性プロポリス固形組成物、その製造方法および雰囲気改良剤に関する。さらに詳しくは、本発明は、蒸発機能性を有し、かつ良好な臭気感覚を安定して与え、雰囲気改良剤などとして有用なプロポリス固形組成物、このものを効率よく製造する方法および上記プロポリス固形組成物からなる雰囲気改良剤に関するものである。

## 【0002】

【従来の技術】 従来より、天然の抗菌性物質や健康増進物質などとして知られているプロポリスは、ミツバチなどの節足動物によって採集されたポプラやマツなどの顕花植物が生産するフラボノイド類やフェノール類に代表される二次代謝産物と、節足動物が産するロウ物質や唾液分泌物との複合物である。このものを食用とする場合には、そのままではあまりに硬くて食用には不適であるため、通常、エチルアルコールや液化炭酸ガスを用いる

抽出法によって溶液食品とするか、あるいは抽出したものを水溶性多糖類と混合して、唾液により容易に分解しやすい固形食品として、食用に供されている。

【0003】 しかしながら、上記抽出法は、良溶媒を使用する無差別抽出法を根本としており、本来、抗菌性能若しくは健康増進機能に関与しないと考えられるロウ物質までも共に抽出されるために、抽出物は有益でない成分を含み、かつ非水溶性が強調されて、食し難い状態となり、しかも水系溶液で不安定となる。したがって、一般に生活用品として利用する場合でも、用途が著しく制限されるのを免れないという問題があった。

【0004】 一方、食品分野においては、プロポリス原塊と水とを接触させることにより、水溶性成分のみを抽出し、食しやすい製品をつくる方法も講じられているが、この方法は、油溶性の有効成分を取り出しえず、かつ水溶性成分の抽出量も少なく、性能的に満足しうる方法とはいえない。

【0005】 このような事情のもとで、本発明者は、先に、成分抽出上の性能面と食しやすさの両方を満足させる方法として、ポリオール・脂肪酸エステル系界面活性剤の親水性溶液ミセルを利用した、いわゆるミセル抽出法による、プロポリス食品組成物およびその製造方法を発明した(特公平 4-66544 号公報)。この技術によると、食しやすいプロポリス食品が得られるとともに、選別選択的抽出機構により、水溶性および油溶性の有効成分を取り出しながら、有益でないロウ物質を包含させない液体プロポリス食品を製造することができる。

【0006】 しかしながら、その系では独特の臭気が強調され、外気との接触が必要条件となる一般生活用品としては難があった。

【0007】 他方、プロポリス固形組成物としては、プロポリス成分抽出液を、低分子固体の麦芽糖の中に封じ込めたアメ製品や、非水溶性のセルロースに含浸させた錠剤製品などがあるが、これらは前述の液体プロポリス食品製品から、持参しやすいという長所だけでつくられているものであり、蒸発機能性を有さず、かつ臭気も悪いして、それだけでは、食品以外の分野への展開は不向きであった。

## 【0008】

【発明が解決しようとする課題】 本発明は、このような事情のもとで、蒸発機能性を有し、かつ良好な臭気感覚を安定して与え、雰囲気改良剤などとして有用なプロポリス固形組成物、このものを効率よく製造する方法および上記プロポリス固形組成物からなる雰囲気改良剤を提供することを目的とするものである。

## 【0009】

【課題を解決するための手段】 本発明者は、前記目的を達成するために鋭意研究を重ねた結果、プロポリス原塊および／またはその抽出残渣、水または水と特定の水溶性溶剤との混合物、界面活性剤および親水性高分子化合

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物を、それぞれ所定の割合で含有する固形組成物が、天然の抗菌性物質、健康増進物質であるプロポリス由来の有効成分を、微量ずつ連続的に蒸散させるといった蒸発機能性を有し、かつ良好な臭気感覚を安定して与え、雰囲気改良剤などとして有用であること、そして、このプロポリス固形組成物は、水または水と特定の水溶性溶剤との混合物に界面活性剤をミセル溶解させてなる溶液に、プロポリス原塊および／またはその抽出残渣を均一分散させ、これに親水性高分子化合物を添加し、均一混合することにより、効率よく製造しうることを見出し、この知見に基づいて本発明を完成するに至った。

【0010】すなわち、本発明は、(A) プロポリス原塊および／またはその抽出残渣、(B) 水単独または水および水と水素結合しうる水溶性溶剤の混合物、(C) 界面活性剤および(D) 親水性高分子化合物を含有し、かつ(A)成分と(B)成分との合計量100重量部当たり、(C)成分の含有量が0.01～25重量部で、(D)成分の含有量が0.1～50重量部であることを特徴とする蒸発機能性プロポリス固形組成物、並びに、この蒸発機能性プロポリス固形組成物からなる雰囲気改良剤を提供するものである。

【0011】また、上記蒸発機能性プロポリス固形組成物は、本発明の方法に従えば、(B) 水単独または水および水と水素結合しうる水溶性溶剤の混合物に(C) 界面活性剤をミセル溶解させてなる溶液と、(A) プロポリス原塊および／またはその抽出残渣とを混合接触させて、分散状態とし、次いで、これに(D) 親水性高分子化合物を添加して、均一混合することにより、製造することができる。

【0012】

【発明の実施の形態】本発明においては、(A)成分としてプロポリス原塊を用いてもよいし、このプロポリス原塊を各種方法により抽出処理して得られた残渣を用いてもよく、またプロポリス原塊と抽出残渣の両方を混合して用いてもよい。プロポリス原塊としては特に制限されず、いかなる由来のものであってもよく、例えばブラジル産、米国産、ドイツ産、中国産など、いずれも用いることができる。

【0013】また、抽出残渣としては特に制限はなく、従来公知の方法によりプロポリス原塊を抽出処理して得られた残渣を用いることができる。この抽出処理残渣としては、例えば水、エチルアルコール、液化炭酸ガスなどを用い、プロポリス原塊を抽出処理して得られたプロポリス残渣、さらには、特公平4-66544号公報に記載されている方法に従って、複数のOH基を有する溶剤にポリオール・脂肪酸エステル系界面活性剤をミセル溶解させてなる系とプロポリス原塊とを接触させたのち、均一溶解している可溶性成分を除去して得た表面に該界面活性剤の一部が吸着しているプロポリス残渣などを挙げることができる。

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【0014】本発明においては、(B)成分として、水単独、または水および水と水素結合しうる水溶性溶剤の混合物が用いられる。ここで、水と水素結合しうる水溶性溶剤の例としては、メチルアルコール、エチルアルコール、n-プロピルアルコール、イソプロピルアルコール、エチレングリコール、ジエチレングリコール、プロピレングリコール、ジプロピレングリコール、1, 3-ブチレングリコール、グリセリン、エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノプロピルエーテル、エチレングリコールモノイソプロピルエーテル、エチレングリコールモノブチルエーテル、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールモノプロピルエーテル、ジエチレングリコールモノイソプロピルエーテル、ジエチレングリコールモノブチルエーテル、プロピレングリコールモノメチルエーテル、プロピレングリコールモノエチルエーテル、プロピレングリコールモノプロピルエーテル、プロピレングリコールモノイソプロピルエーテル、プロピレングリコールモノブチルエーテル、ジプロピレングリコールモノメチルエーテル、ジプロピレングリコールモノエチルエーテル、ジプロピレングリコールモノプロピルエーテル、ジプロピレングリコールモノイソプロピルエーテル、ジプロピレングリコールモノブチルエーテルなどのアルコール系溶剤、エチレングリコールジメチルエーテル、エチレングリコールジエチルエーテル、ジエチレングリコールジメチルエーテル、ジエチレングリコールジエチルエーテル、フルフラール、ジオキサンなどのエーテル系溶剤、アセトン、メチルエチルケトンなどのケトン系溶剤および2-メチルイミダゾリジノンなどの含窒素系溶剤などが挙げられる。これらの水溶性溶剤は単独で用いてもよいし、2種以上を混合して用いてもよい。

【0015】本発明における(C)成分の界面活性剤としては特に制限はなく、アニオン性、ノニオン性、カチオン性および両性界面活性剤のいずれも用いることができる。上記アニオン性界面活性剤の例としては、アルキルアリアルスルホン酸塩類、各種脂肪酸のナトリウム塩、カリウム塩、トリエタノールアミン塩などの石鹸類、アルキル硫酸塩、アルキルポリオキシアルキレンエーテル硫酸塩などの硫酸エステル塩、アルキルリン酸エステル塩、アルキルアリアルリン酸エステル塩、アルキルポリオキシアルキレンエーテルリン酸エステル塩、アルキルアリアルポリオキシアルキレンエーテルリン酸エステル塩などのリン酸エステル塩類およびポリスチレンスルホン酸塩、ポリアクリル酸塩などのポリソープ類などで代表されるものが挙げられ、これらは単独で用いてもよいし、2種以上を組み合わせて用いてもよい。

【0016】ノニオン性界面活性剤の例としては、ソルビタン脂肪酸エステル、ポリオキシエチレンソルビタン

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脂肪酸エステル、グリセリン脂肪酸エステル、ジグリセリン脂肪酸エステル、トリグリセリン脂肪酸エステル、テトラグリセリン脂肪酸エステル、ペンタグリセリン脂肪酸エステル、ヘキサグリセリン脂肪酸エステル、エチレングリコール脂肪酸エステル、ポリオキシエチレングリコール脂肪酸エステル、ショ糖脂肪酸エステル、ジ（グリセリン）ポラート脂肪酸エステルなどの脂肪酸エステル類、アルキルポリオキシアルキレンエーテル、アルキルアリアルポリオキシアルキレンエーテル、ポリオキシエチレングリコール・ポリオキシプロピレングリコールブロックポリマーなどのポリエーテル類、N、N-ジ（ポリオキシアルキレン）アルキルアミン、N、N、N'、N'-テトラ（ポリオキシアルキレン）エチレンジアミンなどの三級化アミン類、および脂肪酸モノアルキロールアミド、脂肪酸ジアルキロールアミドなどのアミド類などで代表されるものが挙げられ、これらは単独で用いてもよいし、2種以上を組み合わせ用いてもよい。

【0017】カチオン性界面活性剤の例としては、テトラアルキルアンモニウム塩、トリアルキル（ $\beta$ -ヒドロキシアルキル）アンモニウム塩、ジアルキルジ（ポリオキシアルキレン）アンモニウム塩などの第四級アンモニウム塩類などで代表されるものが挙げられ、これらは単独で用いてもよいし、2種以上を組み合わせ用いてもよい。また、両性界面活性剤の例としては、トリアルキルベタイン、アルキルイミダゾリンベタインなどのベタイン類およびレシチンなどのリン脂質などで代表されるものが挙げられ、これらは単独で用いてもよいし、2種以上を組み合わせ用いてもよい。本発明においては、この（C）成分の界面活性剤として、特にカルボン酸塩

を含有する高分子アニオン性界面活性剤が好ましい。

【0018】一方、本発明における（D）成分の親水性高分子化合物の例としては、カラギーナン、寒天、デンプン、ポリビニルアルコール、ポリアクリルアミド、ポリエチレンオキシド、カルボキシメチルセルロース、グアーガム、キサントガム、架橋型ポリアクリル酸塩および架橋型ポリアクリルアミドなどが挙げられる。これらは単独で用いてもよいし、2種以上を組み合わせ用いてもよいが、特にカラギーナンが好適である。

【0019】本発明の蒸発機能性プロポリス固形組成物は、前記（A）成分、（B）成分、（C）成分および（D）成分を含有するものであって、（C）成分の界面活性剤の含有量は、（A）成分と（B）成分との合計量100重量部当たり、0.01～25重量部の範囲で選ばれる。この（C）成分の含有量が0.01重量部未満では（A）成分を安定分散させることが困難であり、また25重量部を超えるとプロポリス由来の有効成分の蒸発機能性が著しく阻害される。（A）成分の分散安定性および有効成分の蒸発機能性のバランスなどの面から、この（C）成分の好ましい含有量は、（A）成分と

（B）成分との合計量100重量部当たり、0.1～5重量部の範囲であり、特に0.5～2重量部の範囲が好適である。

【0020】一方、（D）成分の親水性高分子化合物の含有量は、（A）成分と（B）成分との合計量100重量部当たり、0.1～50重量部の範囲で選ばれる。この（D）成分の含有量が0.1重量部未満では組成物の固化が困難であるし、50重量部を超えるとプロポリス由来の有効成分の蒸発機能性が著しく阻害される。組成物の固化および有効成分の蒸発機能性などを考慮すると、この（D）成分の好ましい含有量は、（A）成分と（B）成分との合計量100重量部当たり、0.5～10重量部の範囲であり、特に1～5重量部の範囲が好適である。

【0021】また、（A）成分と（B）成分との含有割合は、重量比で1：999～1：2の範囲にあるのが好ましい。（A）成分が上記範囲より少ないとプロポリス由来の有効成分の量が少なすぎて本発明の目的が達せられないおそれがあるし、上記範囲より多いと（A）成分の分散安定性が悪くなる傾向がみられる。（A）成分と（B）成分のより好ましい含有割合は、重量比で1：99～1：4の範囲であり、特に1：49～1：9の範囲が好適である。

【0022】次に、本発明の蒸発機能性プロポリス固形組成物の製造方法について説明する。本発明の方法においては、まず（B）成分である水単独または水と前記水溶性溶剤との混合物に、（C）成分である界面活性剤を添加してミセル溶解し、さらに（A）成分であるプロポリス原塊および／またはその抽出残渣を添加するか、あるいは界面活性剤と同時に、プロポリス原塊および／またはその抽出残渣を添加する。なお、プロポリス原塊の抽出残渣として、界面活性剤が吸着されているものを用いる際には、その界面活性剤の種類および量にもよるが、上記（C）成分として界面活性剤を添加しなくてもよい場合がある。

【0023】このようにして、プロポリス原塊および／またはその抽出残渣を添加したのち、好ましくは15～200℃、特に好ましくは15～100℃の温度で混合接触させ、分散状態とする。次いで、この分散液をそのままか、あるいは冷却または加熱して、好ましくは0～200℃、特に好ましくは0～100℃の温度に保持し、これに（D）成分である親水性高分子化合物を添加して均一混合し、静置させる。その際、製造装置内で静置させて固形組成物としたのち、装置から排出してもよいし、液体状態のまま装置から排出したのち、包装容器に採って静置させ、固形組成物としてもよい。

【0024】なお、本発明の蒸発機能性プロポリス固形組成物の製造方法と同様の方法により、従来技術（特公平4-66544号公報）に基づくプロポリス抽出成分のみを含むポリオール・脂肪酸エステル系界面活性剤ミ

セル化液体食品に、親水性高分子化合物を添加して均一混合しても、均一な固形組成物が得られず、その上、はじき出された分離液体が著しく臭気を発散することから、製造上および応用上好ましいものは得られない。

【0025】本発明の蒸発機能性プロポリス固形組成物はまた、そのままの状態で見相と接触させるか、若しくは、ファンなどの装置と共に使用すると、各成分の協力作用により、周囲の悪臭を断つと同時に、快適な感じの香りをもたらす雰囲気改良剤として働くので、健康生活上、極めて有用である。

【0026】本発明の蒸発機能性プロポリス固形組成物には、本発明の目的が損なわれない範囲で、所望により、着色剤、防腐剤、酸化防止剤、芳香剤などの各種添加剤を添加することができる。

【0027】

【実施例】次に、本発明を実施例および応用例によりさらに詳細に説明するが、本発明は、これらの例によってなんら限定されるものではない。

【0028】実施例 1

攪拌機、温度計および加熱装置を備えた密閉式反応装置に、水 90 重量部、グリセリン 5 重量部、テトラグリセリンモノオレエート 1 重量部および平均重合度 5000 のポリアクリル酸ナトリウム 0.01 重量部を仕込み、常圧下、40℃で 20 分間攪拌して均一な溶液を調製した。次いで、この溶液中にブラジル産のプロポリス原塊

5 重量部を添加し、30～40℃で攪拌を行い混合接触させて分散状態としたのち、これにカラギーナン〔MRC ポリサッカライド（株）製、商品名：ソアギーナ WX-560〕2.5 重量部を添加し、攪拌しながら 60℃まで昇温して均一混合し、50～60℃で反応装置から排出した。その後、20℃にて 24 時間静置させて、茶褐色の蒸発機能性プロポリス固形組成物を得た。

【0029】この組成物を上部開放容器に入れ、20℃で静置 1 日後および 30 日後の形態および表面の臭気の状態を観測した。結果を表 1 に示す。

【0030】比較例 1

水 90 重量部、グリセリン 5 重量部、テトラグリセリンモノオレエート 1 重量部および平均重合度 5000 のポリアクリル酸ナトリウム 0.01 重量部からなる均一溶液中に、さらにプロポリス抽出成分（抽出溶媒：水 10 重量％、グリセリン 89 重量％およびテトラグリセリンモノオレエート 1 重量％よりなるもの）5 重量部を含有させた溶液に対して、実施例 1 で使用したのと同じカラギーナン 2.5 重量部を添加し、実施例 1 と同様にして均一混合したのち、20℃で 24 時間静置させて、固形組成物を得た。この組成物について、実施例 1 と同様にして評価した。結果を表 1 に示す。

【0031】

【表 1】

表 1

	20℃、1日静置後		20℃、30日静置後	
	形 態	表面臭気	形 態	表面臭気
実施例 1	均一固形	さわやかな香り	均一固形	さわやかな香り
比較例 1	表面に液状物分布	刺激性臭気あり	上部に液相、下部に固相と分離	刺激性臭気強い

【0032】表 1 から、実施例 1 の組成物では、各構成成分が正しく複合化されており、良い雰囲気をつくり出すべく、蒸発機能性が作用していることが分かる。

【0033】実施例 2

攪拌機、温度計、加熱および冷却装置を備えた密閉式反応装置に、水 90 重量部、平均重合度 3000 のポリアクリル酸カリウム 0.01 重量部を仕込み、15℃で 30 分間攪拌を行ったのち、この溶液にブラジル産のプロポリス原塊 10 重量部を添加し、5 kg/cm<sup>2</sup> G の加圧下に 95～100℃で 3 時間、混合接触させて分散状態とした。

【0034】次いで、内温を 0℃まで下げたのち、全量を別の開放式反応装置に移し、攪拌下に、この分散液に架橋型ポリアクリル酸ナトリウム〔昭和電工（株）製、商品名：ビスコメート PX-112〕3 重量部を添加し

10 分間均一混合し、褐色の蒸発機能性プロポリス固形組成物を得た。この組成物について、実施例 1 と同様にして評価した。結果を表 2 に示す。

【0035】比較例 2

水 90 重量部および平均重合度 3000 のポリアクリル酸カリウム 0.01 重量部からなる均一溶液中に、さらにプロポリス抽出成分（抽出溶媒：エチルアルコール）10 重量部を含有させた溶液に対して、実施例 2 で使用したのと同じ架橋型ポリアクリル酸ナトリウム 3 重量部を添加し、実施例 2 と同様にして固形組成物を得た。この組成物について、実施例 1 と同様にして評価した。結果を表 2 に示す。

【0036】

【表 2】

表 2

	20℃, 1日静置後		20℃, 30日静置後	
	形 態	表面臭気	形 態	表面臭気
実施例 2	均一・顆粒状固形	さわやかな香り	約30%分が蒸発して小さくなった顆粒	さわやかな香り
比較例 2	所々に液状物分布	刺激性臭気あり	表面に液体膜ができる	油臭が強くなる

【0037】表2から、実施例2の組成物では、各構成成分が正しく複合化されており、蒸発機能性も順調に作用していることが分かる。

【0038】実施例3～8

表3および表4に示す種類と量の(A)成分、(B)成分、(C)成分および(D)成分を用い、実施例1また

は実施例2と同様にして、蒸発機能性プロポリス固形組成物を製造した。これらの組成物をそれぞれ密閉容器に入れて、20℃で30日間静置後の形態と表面の臭気

【0039】

【表3】

表 3

実施例	(A) 成分	(B) 成分	(C) 成分	(D) 成分	製造方法
3	ブラジル産 プロポリス原塊 7 重量部	水 エチルアルコール 8 0 重量部 1 0 重量部 ジエチレングリコール モノメチルエーテル 3 重量部	ポリ (10) オキシエチレンノニルアフェニル エーテルリン酸アンモニウム 1 重量部 N, N-ジ [ポリ (5) オキシエチレン] ラウリルアミン 1 重量部 平均重合度 2 0 0 0 のステレン-マレイン 酸ナトリウム共重合体 0. 2 重量部	カラギーナン (MRC ポリ サッカライド社製) ソアギーナ WX-560) 4 重量部 グアーガム 1 重量部	実施例 1 の 製造方法に 準じる
4	ブラジル産 プロポリス原塊 4 重量部	水 ジオキサン エチレングリコール メチルエーテル 9 0 重量部 3 重量部 3 重量部	オレイン酸カリウム 0. 3 重量部 ポリ (8) オキシエチレンオクタチル フェニルエーテル 1. 2 重量部 ラウリル硫酸ナトリウム 0. 5 重量部 平均重合度 2 0 0 0 のメタクリル酸 カリウム (9 : 1 モル比) 共重合体 0. 5 重量部	カラギーナン (MRC ポリ サッカライド社製) ソアギーナ MW-351) 5 重量部 キサンタンガム 0. 3 重量部 カルボキシメチルセルロース 0. 2 重量部	同 上
5	米産 プロポリス原塊 1 0 重量部	水 1, 3-ブチレン グリコール アセトン 8 4 重量部 5 重量部 1 重量部	平均分子量 2 0 0 0 のポリプロピレン グリコールの両側に平均分子量 2 0 0 0 のポリエチレングリコールをブロック ポリマー化させたもの 2 4 重量部 平均重合度 6 0 0 0 のアクリルアミド- アクリル酸ナトリウム (1 : 4 モル比) 共重合体 1 重量部	カラギーナン (MRC ポリ サッカライド社製) ソアギーナ MM-301) 3 重量部 デンプン 1 重量部 グアーガム 2 重量部	同 上



表 4

実施例	(A) 成分	(B) 成分	(C) 成分	(D) 成分	製造方法
6	中国産 プロポリス原塊 1 重量部	水 99 重量部	平均重合度 6000 のポリアクリル酸 ナトリウム 0.01 重量部	カラギーナン (MRC ポリサッカラ イド社製ソアギーナ MW-280) 1 重量部 平均重合度 500 の 70% ポリビニルアルコール 29 重量部 平均重合度 2000 のポリエチレン オキシサイド 20 重量部	実施例 1 の 製造方法に 準じる
7	ブラジル産 プロポリス原塊 20 重量部	水 78 重量部 イソプロピルアルコール 1 重量部 フルフラール 0.5 重量部 2-メチルイミダゾリジ ノン 0.5 重量部	ジヘキサデシルジメチルアンモニウム クロリド 0.1 重量部 ドデシルジメチルベタイン 0.1 重量部 レシチン 0.2 重量部 平均重合度 1000 のポリアクリル 酸アンモニウム 0.6 重量部	カラギーナン (MRC ポリサッカラ イド社製ソアギーナ MM-501) 0.05 重量部 精製寒天粉末 0.05 重量部	同 上
8	中国産 プロポリス原塊 5 重量部	水 90 重量部 メタノール 5 重量部	ポリ (10) オキシエチレン グリコールモノラウレート 0.8 重量部 平均重合度 4000 のアクリルアミド -アクリル酸ナトリウム (1:9 モル 比) 共重合体 0.2 重量部	カラギーナン (MRC ポリサッカラ イド社製ソアギーナ WX-560) 0.01 重量部 架橋型ポリアクリル酸ナトリウム (昭和電工 (株) 製ビスコメート PX-112) 0.02 重量部 架橋型ポリアクリル酸ナトリウム- ポリアクリルアミド共重合体 (台湾 製マジッククリスタル 800) 0.07 重量部	実施例 2 の 製造方法に 準じる

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表5

		20℃, 30日静置後	
		形 態	表面臭気
実 施 例	3	均一固形	さわやかな香り
	4	"	"
	5	"	"
	6	"	"
	7	"	"

【0042】表5から、実施例3～8の組成物は、優れた性能を有することが分かる。

#### 【0043】実施例9

ソルビタンモノラウレート1重量部とグリセリン100重量部とからなる溶液と、ブラジル酸プロポリス原塊5重量部とを60～70℃で1時間加熱接触させたのち、ミセル化および溶媒抽出されて均一溶解している部分を除去し、プロポリス抽出残渣を得た。

【0044】攪拌機、温度計、加熱及び冷却装置を備えた開放式反応装置に、上記プロポリス抽出残渣（プロポリス残渣6重量部とそれに付着しているソルビタンモノラウレート0.04重量部およびグリセリン4重量部からなる複合物）を仕込んだのち、水85重量部、エチルアルコール5重量部および平均重合度5000のポリアクリル酸ナトリウム0.01重量部を仕込み、常圧下、20℃で均一混合した。次いで、徐々に加熱しながら、

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これにカラギーナン〔MRCポリサッカライド（株）製、商品名：ソアギーナWX-560〕5重量部を添加して、60℃まで昇温したのち、同温度で反応装置から排出し、20℃で24時間静置させて、茶褐色の蒸発機能性プロポリス固形組成物を得た。この組成物について、実施例1と同様にして評価した。結果を表6に示す。

#### 【0045】実施例10

テトラグリセリンモノオレエート1重量部とプロピレングリコール100重量部からなる溶液と、中国産プロポリス原塊5重量部とを60～70℃で30分間加熱接触させたのち、ミセル化抽出されて均一溶解している部分を除去し、プロポリス抽出残渣を得た。

【0046】攪拌機を備えた開放式反応装置に、上記プロポリス抽出残渣（プロポリス残渣9重量部とそれに付着しているテトラグリセリンモノオレエート0.01重量部およびプロピレングリコール1重量部からなる複合物）を仕込んだのち、水90重量部を仕込み、20℃で攪拌を行い、均一混合した。次いで、これに架橋型ポリアクリル酸ナトリウム〔昭和電工（株）製、商品名：ビスコメートPX-112〕3重量部を添加して15分間均一に混合し、褐色の蒸発機能性プロポリス固形組成物を得た。この組成物について、実施例1と同様にして評価した。結果を表6に示す。

#### 【0047】

#### 【表6】

表6

	20℃, 1日静置後		20℃, 30日静置後	
	形 態	表面臭気	形 態	表面臭気
実施例 9	均一固形	さわやかな香り	約20%分が蒸発して小さくなった均一固形	さわやかな香り
実施例 10	均一顆粒状固形	さわやかな香り	約30%分が蒸発して小さくなった顆粒	さわやかな香り

【0048】表6から、実施例9および10の組成物は、各構成成分が正しく複合化されており、かつ蒸発機能性も確実に作用していることが分かる。

#### 【0049】応用例1

自動車を運転する20～60才の男女120名を無作為に選り対象者とした。実施例1～10で得られた蒸発機能性プロポリス固形組成物および比較例1、2で得られた固形組成物それぞれ100gを、直径6cm、高さ6cmの上部開放円筒容器に充填して、排気量1800～3000ccの試験用乗用車の前部座席中央位置に固定し、その際の臭気感覚および運転時の気分についてのパネルテストを、以下示す要領に従って実施した。結果を表7に示す。

#### 【0050】（1）臭気感覚

1年以上にわたって1日平均3時間走行させていた試験

用乗用車に、各組成物を固定し、ドアおよび窓をすべて閉めて、室温条件で24時間無人のまま停止させた状態としたのち、前部座席側のドアを開き、1種の組成物について10人の対象者に車内の臭気を嗅がせて、解答してもらった。

#### 【0051】（2）運転時の気分

1年以上にわたって1日平均3時間走行させていた試験用乗用車に各組成物を固定し、ドアおよび窓をすべて閉めて、室温状態で24時間、無人のまま停止させた状態としたのち、1種の組成物を取付けた試験用乗用車について10人の対象者に3時間乗ってもらい（ただし、1時間15分走行→30分間停止→1時間15分走行とした）、解答してもらった。

#### 【0052】

#### 【表7】

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表 7

試 料	臭気感覚 ※1	運転時の気分 ※2
実施例 1	A	◎
実施例 2	A	◎
実施例 3	A	◎
実施例 4	A	◎
実施例 5	A	◎
実施例 6	A	◎
実施例 7	A	◎
実施例 8	A	◎
実施例 9	A	◎
実施例 10	A	◎
比較例 1	D	△
比較例 2	D	△

## 【0053】〔注〕

※1 臭気感覚の評価基準は、以下のとおりである。

A・・・10人の試験者全員が、従来あった車内臭がなく  
なり、好ましい臭いになったとしているもの。

B 10人の試験者中1～3人が、従来と変わらないと感じ、他の9～7人が好ましい臭いになったとしているもの。

C・・・10人の試験者中4～6人が、従来と変わらないと感じ、他の6～4人が変わった臭気になったとしているもの。

D・・・10人の試験者中7～9人が臭気が強すぎて好ましくないと感じ、それ程でもないと感じている者が3人以下のもの。

【0054】※2 運転時の気分の評価基準は、次のとおりである。

◎・・・10人の試験者全員が、以前より気分良く運転できるとしたもの。

○・・・10人の試験者中7～9人が、以前より気分良く運転できるようになったとしているもの。

△・・・10人の試験者中、以前より気分良く運転できるとした者が6人以下のもの。

表7から明らかなように、本発明の蒸発機能性プロポリス固形組成物は、臭気感覚および運転時の気分共に良好となり、乗用車内の雰囲気改良剤として非常に優れているものであることが分かる。

## 【0055】応用例2

慢性的な鼻炎の症状を有する15～65才の男女120名を無作為に選び対象者とした。実施例1～10で得られた蒸発機能性プロポリス固形組成物および比較例1、2で得られた固形組成物それぞれ300gを、上部中央に直径2.2cmの穴を開けた直径7.2cm、高さ8.8cmの円筒容器に充填して、モーターおよびシロッコファンを内蔵する送風機（台湾製AIR FRESH SURE、8.5cm×9cm×24cm）に取り付け、試験者の就寝時に頭部から50cmの位置に固定して、1日平均8時間送風機を作動させた状態での臭気感覚および呼吸の際の気分についてのパネルテストを、以下に示す要領に従って実施した。結果を表8に示す。

## 【0056】（1）臭気感覚

各組成物を取り付けた送風機を作動させた第1日目の15分後に、1種の組成物について10人の対象者に寝入り前に頭部付近の臭気を嗅がせて、解答してもらった。

## （2）呼吸の際の気分

各組成物を取り付けた送風機を夜間1日平均8時間ずつ作動させた30日後の眠覚め時に、1種の組成物について10人の対象者に深呼吸してもらい、解答してもらった。

## 【0057】

## 【表8】

表 8

試 料	臭気感覚 ※1	運転時の気分 ※2
実施例 1	A	◎
実施例 2	A	◎
実施例 3	A	◎
実施例 4	A	◎
実施例 5	A	◎
実施例 6	A	◎
実施例 7	A	◎
実施例 8	A	◎
実施例 9	A	◎
実施例 10	A	◎
比較例 1	D	△
比較例 2	D	△

## 【 0 0 5 8 】 【 注 】

※ 1 臭気感覚の評価基準は、以下のとおりである。

A・・・10人の試験者全員が好ましい臭いであるとしているもの。

B・・・10人の試験者中1～3人が臭気が強すぎて好ましくないと感じ、他の9～7人が好ましい臭いになったとしているもの。

C・・・10人の試験者中4～6人が臭気が強すぎて好ましくないと感じ、他の6～4人がそれ程でもないとしているもの。

D・・・10人の試験者中7～9人が臭気が強すぎて好ましくないと感じ、それ程でもないとしている者が3人以下のもの。

【 0 0 5 9 】 ※ 2 呼吸の際の気分の評価基準は、次のとおりである。

◎・・・10人の試験者全員が、送風機の設置、作動前より気分良く呼吸できるようになったとしているもの。

○・・・10人の試験者中7～9人が、送風機の設置、作動前より気分良く呼吸できるようになったとしているもの。

△・・・10人の試験者中、送風機の設置、作動前より気

分良く呼吸できるようになったと感じている者が6人以下のもの。

20 表 8 から明らかなように、本発明の蒸発機能性プロポリス固形組成物は、臭気感覚、呼吸の際の気分共に感じがよく、室内の雰囲気改良剤として非常に優れているものであることが分かる。

## 【 0 0 6 0 】

【発明の効果】本発明の蒸発機能性プロポリス固形組成物は、プロポリスの有効成分と担体成分とを分離させない原塊のまま、あるいはその抽出残渣の形で、界面活性剤の水系ミセル溶液と混合接触させて得た均一分散液を親水性高分子化合物で固形化したものであって、組成的に安定な固形物となり、蒸発成分が規則正しく、かつ連続的に蒸散し、良好な臭気感覚を与え、雰囲気改良剤などとして有用である。

30 【 0 0 6 1 】したがって、本発明を実施することにより、プロポリスのもつ天然の抗菌性物質および健康増進物質としての役割を、従来の飲用健康食品としての用途のみでなく、新たに、環境へ設置する生活用品として応用することも可能にする。

## 【 手続補正書 】

【提出日】平成 1 0 年 9 月 2 2 日

【手続補正 1】

【補正対象書類名】明細書

【補正対象項目名】0 0 3 9

【補正方法】変更

## 【補正内容】

【 0 0 3 9 】

【表 3】

表 3

実施例	(A) 成分	(B) 成分	(C) 成分	(D) 成分	製造方法
3	ブラジル産 プロポリス原塊 7 重量部	水 8 0 重量部 エチルアルコール 1 0 重量部 ジエチレングリコール モノメチルエーテル 3 重量部	ポリ (10) オキシエチレンノニルフエニル エーテルリン酸アンモニウム 1 重量部 N, N-ジ [ポリ (5) オキシエチレン] テウリルアミン 1 重量部 平均重合度 2 0 0 0 のスチレン-マレイン 酸ナトリウム共重合体 0. 2 重量部	カラギーナン (MRCポリ サッカライド社製) ソアギーナ WX-660) 4 重量部 グアーガム 1 重量部	実施例 1 の 製造方法に 準じる
4	ブラジル産 プロポリス原塊 4 重量部	水 8 0 重量部 ジオキサン 3 重量部 エチレングリコール メチルエーテル 3 重量部	オレイン酸カリウム 0. 3 重量部 ポリ (8) オキシエチレンオクチルフエニル エーテル 1. 2 重量部 ラウリル硫酸ナトリウム 0. 5 重量部 平均重合度 2 0 0 0 のメタクリル酸メチル- メタクリル酸カリウム (9 : 1 モル比) 共重合体 0. 5 重量部	カラギーナン (MRCポリ サッカライド社製) ソアギーナ MW-351) 5 重量部 キサンタンガム 0. 3 重量部 カルボキシメチルセルロース 0. 2 重量部	同 上
5	米國産 プロポリス原塊 1 0 重量部	水 8 4 重量部 1, 3-ブチレン グリコール 5 重量部 アセトン 1 重量部	平均分子量 2 0 0 0 のポリプロピレングリ コールの両側に平均分子量 2 0 0 0 のポリ エチレングリコールをブロックポリマー化 させたもの 2 4 重量部 平均重合度 6 0 0 0 のアクリルアミド- アクリル酸ナトリウム (1 : 4 モル比) 共重合体 1 重量部	カラギーナン (MRCポリ サッカライド社製) ソアギーナ MM-301) 3 重量部 デンプン 1 重量部 グアーガム 2 重量部	同 上

【手続補正 2】

【補正対象書類名】明細書

【補正対象項目名】0041

【補正方法】変更

【補正内容】

【0041】

【表 5】

表 5

		20℃, 30日静置後	
		形 態	表面臭気
実 施 例	3	均一固形	さわやかな香り
	4	〃	〃
	5	〃	〃
	6	〃	〃
	7	〃	〃
	8	〃	〃